

WATTS

DICTIONARY OF CHEMISTRY.

REVISED, AND ENTIRELY REWRITTEN (1894)

BY

M. M. PATTISON MUIR, M.A.

FORMERLY FELLOW, AND PRÆLECTOR IN CHEMISTRY, OF GONVILLE AND CAIUS
COLLEGE, CAMBRIDGE

AND

H. FORSTER MORLEY, M.A., D.Sc.

FELLOW OF UNIVERSITY COLLEGE, LONDON. AND LECTURER ON PHYSICS AND
CHEMISTRY AT CHARING CROSS HOSPITAL MEDICAL SCHOOL

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INTRODUCTION*
TO THE ARTICLES ON INORGANIC CHEMISTRY.

It has been thought advisable to include in an ADDENDA brief accounts of the chief work done in descriptive inorganic chemistry since the publication of Vols. I., II., and III., and the printing off the final proofs of Vol. IV.

Nothing bearing on organic chemistry has been included in the ADDENDA, as to give an account of what has been done in this department since the various volumes were published would occupy many hundred pages.

Dates are attached to the references made to original memoirs in the ADDENDA; and references are frequently made to abstracts of the memoirs in the *Journal of the Chemical Society*.

M. M. PATTISON MUIR.

INTRODUCTION

TO THE ARTICLES RELATING TO ORGANIC CHEMISTRY.

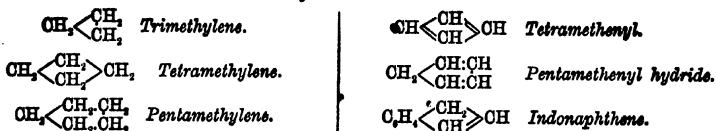
THE NAMES used to denote ring formulae are given below for convenience of reference.*

Since the publication of the last volume I have been assisted in the work of reading and making abstracts of original memoirs by Drs. T. Cooksey, T. A. Lawson, Samuel Rideal, Messrs. J. Wilkie, G. N. Huntly, and J. T. Norman. I have also been assisted by Mr. Arthur G. Green and Mr. Cecil W. Cunningham in the work of revising the proof-sheets. I have great pleasure in thanking these gentlemen for the energetic and efficient manner in which they have carried out their share of the work.

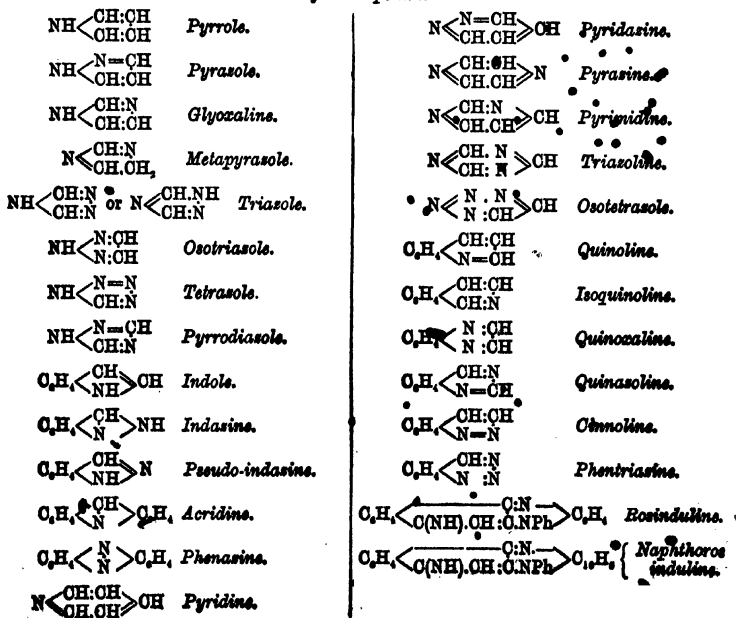
H. FORSTER MOSELEY.

Nomenclature of Ring Formulae.

Hydrocarbons.

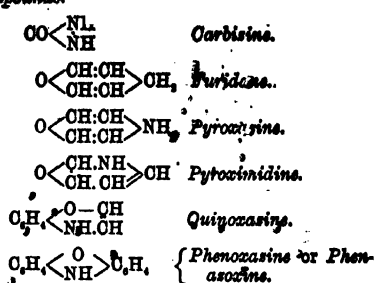
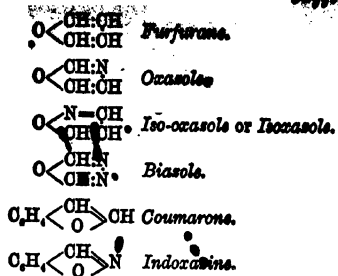


Nitrogen compounds.

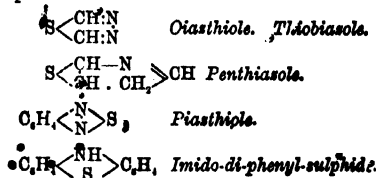
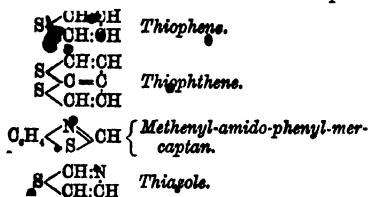


INTRODUCTION

Oxygen compounds.



Sulphur compounds.



INITIALS OF SPECIAL CONTRIBUTORS.

S. A.	SVANTE ARRHENIUS, <i>Ph.D., Professor of Chemistry in Stockholm.</i> Contributes SOLUTIONS I.
J. W. O.	J. W. CAPSTICK, D.Sc., M.A., <i>Fellow of Trinity College, and Demonstrator in Physics in the University, Cambridge.</i> Contributes CAPILLARITY, METHODS BASED ON; and VISCOSITY OF LIQUIDS.
G. G.	GEORGE GLADSTONE, Esq. Contributes OPTICAL METHODS, section Refraction and Dispersion.
W. D. H.	W. D. HALLIBURTON, M.D., F.R.S., <i>Professor of Physiology at King's College, London.</i> Contributes PROTEIDS.
W. N. H.	W. N. HARTLEY, F.R.S., <i>Professor of Chemistry in the Royal College of Science Dublin.</i> Contributes OPTICAL METHODS, section Spectroscopic methods.
E. A. L.	E. A. LETTS, Ph.D., <i>Professor of Chemistry at Queen's College, Belfast.</i> Contributes PHOSPHINES.
R. M.	RAPHAEL MELDOLA, F.R.S., <i>Professor of Chemistry in the Finsbury Technical College.</i> Contributes PHOTOGRAPHIC CHEMISTRY.
W. O.	WILHELM OSTWALD, Ph.D., <i>Professor of Chemistry in the University of Leipzig.</i> Contributes ELECTRICAL METHODS.
C. O'S.	CORNELIUS O'SULLIVAN, F.R.S., <i>Burton-on-Trent.</i> Contributes STARCH and SUGARS.
S. U. P.	SPENCER PICKERING, M.A., F.R.S. Contributes SOLUTIONS II.
S. R.	SAMUEL RIDEAL, D.Sc. Contributes TANNIN.
W. A. T.	WILLIAM A. TILDEN, D.Sc., F.R.S., <i>Professor of Chemistry at the Royal College of Science, South Kensington.</i> Contributes TERPENES.
T. E. T.	T. E. THORPE, D.Sc., Ph.D., F.R.S., <i>Head of the Government Laboratories, Somerset House.</i> Contributes SPECIFIC VOLUMES.

Articles by Mr. MUIR are initialed M. M. P. M.

Unsigned ARTICLES are by Dr. MORLEY, except those in the Addenda, which are by Mr. MUIR.

ABBREVIATIONS

1. JOURNALS AND BOOKS.

When an author has been mentioned in an article, he is usually referred to thereafter in that article by his initials only.

<i>A.</i>	Liebig's <i>Annales</i> der Chemie.
<i>A. A.</i>	<i>Annales de la Sociedad Científica Argentina.</i>
<i>Ann. Ch.</i>	<i>Annales de Chimie et de Physique.</i>
<i>P. Am. A.</i>	Proceedings of the American Academy of Arts and Sciences.
<i>Am.</i>	American Chemical Journal.
<i>Ann. M.</i>	<i>Annales des Mines.</i>
<i>Am. S.</i>	American Journal of Science.
<i>A. C. J.</i>	Journal of the American Chemical Society.
<i>Am. Ch.</i>	American Chemist.
<i>Am. J.</i>	American Journal of Pharmacy.
<i>a Pharm.</i>	
<i>An.</i>	The Analyst.
<i>A. Ph. S.</i>	Proceedings of the American Philosophical Society.
<i>Ar. N.</i>	Archives néerlandaises—The Hague.
<i>Acad.</i>	Mémoires de l'Académie des Sciences.
<i>Ar. Ph.</i>	Archiv der Pharmacie.
<i>Ar. Sc.</i>	Archives des Sciences phys. et nat.
<i>B.</i>	Berichte der deutschen chemischen Gesellschaft.
<i>B. A.</i>	Reports of the British Association.
<i>Bl.</i>	Bulletin de la Société chimique de Paris.
<i>B. B.</i>	Berliner Akademie-Berichte.
<i>B. C.</i>	Biedermann's Centralblatt für Agricultur-Chemie.
<i>B. J.</i>	Berzelius' Jahresberichte.
<i>B. M.</i>	Berliner Monatsberichte.
<i>C. & Mem.</i>	Memoirs of the Chemical Society of London.
<i>C. J.</i>	Journal of the Chemical Society of London.
<i>C. J. Proc.</i>	Proceedings of the Chemical Society of London.
<i>C. N.</i>	Chemical News.
<i>C. R.</i>	Comptes-rendus hebdomadaires des Séances de l'Académie des Sciences—Paris.
<i>C. C.</i>	Chemisches Central-Blatt.
<i>D. P. J.</i>	Dingler's polytechnisches Journal.
<i>Fr.</i>	Fresenius' Zeitschrift für analytische Chemie.
<i>G.</i>	Gazzetta chimica italiana.
<i>G. A.</i>	Gilbert's Annalen der Physik und Chemie.
<i>H.</i>	Hoppe-Seyler's Zeitschrift für physiologische Chemie.
<i>I.</i>	Proceedings of the Royal Irish Academy.
<i>J.</i>	Jahresbericht über die Fortschritte der Chemie und verwandter Wissenschaften.
<i>J. C. T.</i>	Jahresbericht für Chemische Technologie.
<i>J. M.</i>	Jahrbuch für Mineralogie.
<i>J. de Ph.</i>	Journal de Physique et des Sciences accessoires.
<i>J. Ph.</i>	Journal de Pharmacie et de Chimie.
<i>J. pr.</i>	Journal für praktische Chemie.
<i>J. Th.</i>	Jahresbericht über Thierchemie.
<i>J. R.</i>	Journal of the Russian Chemical Society.
<i>J. Z.</i>	Jenaische Zeitschrift für Medizin und Naturwissenschaft.
<i>L. V.</i>	Landwirthschaftliche Versuchs-Stationen.
<i>M.</i>	Monatshefte für Chemie und verwandte Theile anderer Wissenschaften.
<i>M. S.</i>	Le Moniteur Scientifique.
<i>Mém. S.</i>	Mémoires de la Société d'Arsueil.
<i>M. A.</i>	
<i>Mém. B.</i>	Mémoires couronnés par l'Académie de Bruxelles.

ABBREVIATIONS

N.	Nature.
N. Ed. P. J.	New Edinburgh Philosophical Journal.
N. J. P.	Neues Jahresbericht der Pharmacie.
N. R. P.	Neues Repertorium für die Pharmacie.
N. J. T.	Neues Journal von Trommsdorff.
P. M.	Philosophical Magazine.
P.	Poggendorf's Annalen der Physik und Chemie.
P. B.	Beiblätter zu den Annalen der Physik und Chemie.
Pf.	Pflüger's Archiv für Physiologie.
Pr. E.	Proceedings of the Royal Society of Edinburgh.
Ph.	Pharmaceutical Journal and Transactions.
Ph. C.	Pharmaceutisches Centralblatt.
Pr.	Proceedings of the Royal Society.
P. R. I.	Proceedings of the Royal Institution of Great Britain.
P. Z.	Pharmaceutische Zeitschrift für Russland.
R. T. C.	Recueil des travaux chimiques des Pays-Bas.
R. P.	Repertorium für die Pharmacie.
Q. J. S.	Quarterly Journal of Science.
S.	Schweigger's Journal der Physik.
Scher. J.	Scherer's Journal der Chemie.
S. C. I.	Journal of the Society of Chemical Industry.
Sitz. W.	Sitzungsberichte der K. Akademie zu Wien.
T. or Tr.	Transactions of the Royal Society.
T. E.	Transactions of the Royal Society of Edinburgh.
W.	Wiedemann's Annalen der Physik und Chemie.
W. J.	Wagner's Jahresbericht.
Z.	Zeitschrift für Chemie.
Z. B.	Zeitschrift für Biologie.
Z. f. d. g. Naturwiss.	Zeitschrift für die gesammten Naturwissenschaften.
Z. K.	Zeitschrift für Krystallographie und Mineralogie.
Z. P. C.	Zeitschrift für physikalische Chemie.
Bn.	Handbuch der organischen Chemie: von F. Beilstein, 2te Auflage.
E. P.	English Patent.
G. P.	German Patent.
Gm.	Gmelin's Handbook of Chemistry—English Edition.
Gm.-K.	Gmelin-Kraut: Handbuch der anorganischen Chemie.
Gerh.	Traité de Chimie organique: par Charles Gerhardt.
K.	Lehrbuch der organischen Chemie: von Aug. Kekulé.
S. O.	Graham-Otto: Lehrbuch der anorganischen Chemie [5th Ed.]
Stas.	Stas' Recherches, &c.
Rech.	Aronstein's German translation referred to as Chem. Proport.
Stas.	
Nouv. R.	Stas' Nouvelles Recherches, &c.
Th.	Thomsen's Thermochemische Untersuchungen.

II. TERMS AND QUANTITIES, &c., FREQUENTLY USED.

Aq.	Water; e.g. NaOH _{aq} means an aqueous solution of caustic soda.
aq.	18 parts by weight of water.
A	Residues of mono-, di-, and tri-basic acids. Thus, in describing the salts of a monobasic acid NaA', CaA', AlA', may be written, HA' standing for the acid. For a dibasic acid we should write Na ₂ A'', CaA'', Al ₂ A'', &c.
A'	
A''	
A'''	Stand for bases of the ammonia type, in describing their salts. Thus the hydrochloride would be B'HCl or B''2HCl, according as the base is monacid or diacid, &c.
B' B'' etc.	
conc.	Concentrated.
dil.	Dilute.
g.	gram.
mgm.	milligram.
mm.	millimetre.
mol.	molecule.
oil.	liquid, nearly, or quite, insoluble in water.
pp.	precipitate.
to ppt.	to precipitate.
ppg.	precipitating.
ppd.	precipitated.

ABBREVIATIONS

M. M.	Molecular magnetic rotatory power = $\frac{m \times \alpha}{d \times \alpha' \times m'}$, where m = molecular weight of the body of S.G. = d , α = angle of rotation under magnetic influence, α' = angle of rotation of water under same influence, and m' = molecular weight of water (18).
Ac	Acetyl C ₂ H ₃ O
Bz	Benzoyl C ₆ H ₅ O
Cy	Cyanogen CN
Et	Ethyl C ₂ H ₅
Me	Methyl CH ₃
Ph	Phenyl C ₆ H ₅
Pr	Normal Propyl CH ₂ CH ₂ CH ₃
Pr	Isopropyl CH(CH ₃) ₂
R, R' &c.	Alcohol radicals or alkyls.
prim.	primary.
sec.	secondary.
tert.	tertiary.
n.	normal.
m, o, p	meta—ortho—para.
c	consecutive.
i	irregular.
s	symmetrical.
as	unsymmetrical.
ψ	pseudo.
N	attached to nitrogen.
α, β, γ	Employed to denote that the substituent is attached to a carbon atom which is next, next but one, or next but two, respectively, to the terminal carbon atom. The end to be reckoned from is determined by the nature of the compound. Thus CH ₃ CHBrCO ₂ H is α-bromopropionic acid.
γ	denotes that the element or radicle which follows it is attached to a terminal carbon atom.
α, β, γ, &c.	indicate position in an open chain, only.
1, 2, 3, &c.	indicate position in a ring only.
(α), (β), &c.	Used when α, β, &c. are employed in a sense different from the above, e.g. (α)-di-bromo-camphor.
(B.)	Baeyer's Nomenclature:
(Py.)	benzene ring.
	pyridine ring.
	Thus (B. 1:3) dichloroquinoline, means a meta-dichloroquinoline in which the chlorine atoms are both in the benzene ring.
	While (Py. 1:3) dichloroquinoline, means a similar body, only the chlorine atoms are in the pyridine ring. The numbers are counted from two carbon atoms which are in different rings; but, both united to the same carbon atom.
(A.)	denotes the central ring in the molecule of anthracene, acridines, and azines.
exo	means that the element or radicle it precedes is in a closed ring.
endo	not in a benzene ring.
allo	denotes "isomerism" that is not indicated by ordinary formulae; thus maleic acid may be called <i>allo</i> -fumaric acid.
thio	denotes displacement of oxygen by sulphur.
sulpho	" the group SO ₂ H, except in the word sulphocyanide.
sulphydro	" the group SH.
	Tribromonitrobenzene sulphonic acid [T:2:3:4:5] means that the three bromines occupy positions 1, 2, and 3; the nitro-group the position 4, and the sulpho-group the position 5.

* Denotes that the formula to which it is affixed has not been determined by analysis. But it by no means follows that formulae without this mark are those analysed compounds.

All temperatures are given in degrees Centigrade unless when specially stated otherwise.

Wave-lengths are given in 10⁻³ mm.

Formulae, when used instead of names of substances, have a qualitative meaning only.

Thomson's notation is used in thermochemical data.

DICTIONARY OF CHEMISTRY

PHENYL-AZOXAZOLE $\text{CH}_3\text{N}=\text{O}$. [30°].

Formed by the action of CO , on an alkaline solution of the oxim of phenyl-glyoxal (Ruggano, *B.* 24, 3508). Needles, insol. water.

PHENYL-BENZAMIDINE $\text{C}_6\text{H}_5\text{N}$, i.e. $\text{C}_6\text{H}_5\text{C}(\text{NH})\text{NHPh}$ or $\text{C}_6\text{H}_5\text{C}(\text{NPh})\text{NH}_2$. [112°]. Formed from benzonitrile and aniline hydrochloride at 290° (Bernthsen, *A.* 184, 348; 192, 33). Formed also from benzimido-ether and aniline, and from $\text{C}_6\text{H}_5\text{Cl}:\text{NPh}$ and NH_3 (Kobbert, *A.* 265, 188). Nodules (from alcohol), sl. sol. water. Forms a crystalline nitrate.

Reactions.—1. Split up by heat into aniline and benzonitrile.—2. Dry H_2S at 180° forms $\text{C}_6\text{H}_5\text{CS.NHPh}$ and some thio-benzamide.—3. CS_2 at 100° forms thio-benzanilide and phenyl-benzamidine sulphocyanide.—4. Reduced by sodium-amalgam to $\text{C}_6\text{H}_5\text{CH}(\text{NH}_2)\text{NHPh}$.—5. Nitrous acid forms benzanilide (Mieran, *A.* 265, 141).

The derivatives $\text{C}_6\text{H}_5\text{C}(\text{N.SO.Ph})\text{NHPh}$ [189°] and $\text{C}_6\text{H}_5(\text{SO.N:C}(\text{NHPh})\text{C}_6\text{H}_5)$, [196°] have been prepared (Wallach, *A.* 214, 214; Jackson, *Am.* 97, 346).

p-Di-phenyl-benzamidine $\text{C}_{12}\text{H}_{11}\text{N}$, i.e. $\text{C}_6\text{H}_5\text{C}(\text{NPh})\text{NHPh}$. [144°].

Formation.—1. From benzanilide by treatment with PCl_5 and aniline (Gerhardt, *A.* 108, 219; Hofmann, *S.* 1866, 161; Wallach, *A.* 184, 88).—2. From Ph.COCl and aniline with or without ZnCl_2 (Limpricht, *A.* 135, 82; Döbner, *B.* 15, 258).—3. A product of the action of aniline hydrochloride at 250° on benzonitrile, thiobenzamide, or phenyl-benzamidine (Bernthsen, *A.* 184, 352).—4. By heating benzanilide with phenyl cyanate at 190° (Kühn, *B.* 18, 1476).—5. By heating the hydrochloride of benzimido-ether in alcohol with aniline for a long time (Kobbert, *A.* 265, 155).

Properties.—Needles (from alcohol), m. sol. benzene. Its alcoholic solution is neutral to litmus. Not affected by nitrous acid. Split up into aniline and benzanilide when boiled for a long time with alcohol.

Reactions.—1. Dry H_2S at 160° forms thio-benzanilide.—2. CS_2 at 140° forms PhCS.NHPh and NPhCS (Bernthsen, *A.* 192, 34).—3. Conc. HClAq at 190° yields aniline and benzoic acid.

Salts.— B'HCl ; v. sl. sol. water.— B'H.PtCl_4 .— $\text{B'G.N}_2\text{O}_5$; yellow needles.

p-Di-phenyl-benzimidine $\text{C}_{12}\text{H}_{11}\text{N}$, [112°]. Formed by heating diphenylamine hydrochloride with benzonitrile for 5 days (Bernthsen, *A.* 192, 5). Crystalline tablets, v. sl. alcohol and benzene.

Its alcoholic solution turns litmus blue. Conc. H_2SO_4 gives a violet blue colour on warming.

Reactions.—1. Dilute HClAq at 180° forms NPh.Bs .—2. The free base and its hydrochloride yield benzonitrile and diphenylamine on heating.—3. Nitrous acid forms NPh.Bs (Klobbert, *A.* 265, 157).—4. H_2S at 180° forms PhCS.NH_2 , diphenylamine, PhCS.NPh , and NH_3 .—5. CS_2 at 140° forms PhCS.NPh and HNCS .

Salts.— B'HCl . [α . 223°]. Monoclinic crystals, $a:b:c = 529:1:507$; $\beta = 85^\circ 52'$. V. sol. water, sol. alcohol, insol. ether.— B'H.PtCl_4 .— B'HNCS . [203°]. Yellow prisms.

PHENYL-BENZAMIDOXIM

$\text{C}_6\text{H}_5\text{C}(\text{NOH})\text{NHPh}$. [186°]. Formed by boiling $\text{C}_6\text{H}_5\text{CS.NHPh}$ with an alcoholic solution of hydroxylamine (Müller, *B.* 19, 1669). Needles (from water). Yields B'EtCl . ClOOC.Et forms $\text{C}_6\text{H}_5\text{N}_2\text{O}_5$. [167°].

DI-PHENYL-BENZAZIDINE $\text{C}_{12}\text{H}_{11}\text{N}$, i.e. $\text{C}_6\text{H}_5\text{C}(\text{N.NHPh})\text{NH.NHPh}$. [179°]. Formed by the action of phenyl-hydrazine on PhCOCl , or on the hydrochloride of benz-imido-ether dissolved in absolute alcohol (Pinner, *B.* 17, 189; Marckwald, *C.* 1898, 1410). Dark-red needles.

PHENYL-BENZENE v. DIPHENYL

p-Di-phenyl-benzene $\text{C}_{12}\text{H}_{10}$, i.e. $\text{C}_6\text{H}_5\text{Ph}$. Mol. w. 280. [207°]. (α . 405°).

Formation.—1. A product of the action of sodium on an ethereal solution of p-di-bromobenzene, or, better, of a mixture of p-di-bromobenzene with bromine (Riese, *Z.* [3] 6, 192, 785; *A.* 164, 168).—2. Together with its isomeride, and other products, by passing the vapour of benzene, or of a mixture of benzene and toluene, through a red-hot tube (G. Schults, *B.* 6, 415; *A.* 174, 280; 208, 118; Carnelley, *C.* J. 37, 712).—3. Together with the isomeride and other products, by the action of AlCl_3 on a mixture of MeCl and diphenyl (Adam, *B.* [3] 49, 97; *A.* Oh. [6] 15, 241).

Properties.—Needles (from benzene), or iridescent laminae (by sublimation); insol. alcohol, v. sl. sol. HOAc . Its solution in benzene shows blue fluorescence. Conc. H_2SO_4 gives a dirty-green solution changing to purple. CrO_3 in HOAc oxidises it to diphenyl p-carboxylic [216°] and terephthalic acids. Does not form a compound with picric acid. Not volatile with steam. Yields C_{10}Cl_6 on exhaustive chlorination with SbCl_5 (Merr, *A.* Weith, *B.* 16, 2684).

References.—Bromo- and Tri-oxides. Di-phenyl-benzene.

Isodiphenyl-benzene $\text{C}_{12}\text{H}_{10}$, [185°]. (α . 376°). Formed as above. Slander prisms, v. sol. al.

other MeA' (35-36°).

Tri-phenyl-benzene C_6H_5 , i.e. C_6H_5 . Mol. w. 206. [124°] (above 360°). Formed from acetophenone by treatment with P_2O_5 with alcoholic NH_3 , or with dry HCl (Engle, B. 6, 688; 7, 3128). Formed also by heating $C_6H_5CO_2H$ with KOH (Gabriel & Michael, B. 11, 1007). It is also a by-product in the action of acetophenone on dimethylaniline in presence of $ZnCl_2$ (Döbner & Petasch, A. 242, 336). Trimetric crystals; $a:b:c = 566:1:766$, sol. alcohol. Yields benzoic acid on oxidation by CrO_3 in $HOAc$ (Mellin, B. 23, 2633). By exhaustive chlorination with $SbCl_5$ it yields perchloro-triphenyl-benzene (Merz & Weith, B. 18, 2883). On heating with I and red P at 275° it yields the crystalline dodeca-hydrate $C_{12}H_{12}$, and finally oily $C_{12}H_{12}$ (Mallin, B. 23, 2584). Fuming H_2SO_4 at 100° forms a disulphonic acid, which yields the Ba salt $C_{12}H_8O_6Ba$ crystallising in needles.

PHENYL-BENZENE-SULPHAZIDE v. *Phenyl-hydrazide of BENZENE SULPHONIC ACID*.

DI-PHENYL-BENZYL-DI-UREA $NHPh.CO.NH.CPh.N.CO.NHPh$. [172°]. Formed from benzamidine hydrochloride, phenyl cyanate, and $NaOHAq$ (Pinner, B. 22, 1607). Needles, insol. water, v. al. sol. hot alcohol.

PHENYL-BENZYLIMIDO-ETHER $C_{11}H_{11}NO$ i.e. $OPh(NPh).OEt$. A product of the action of aniline on benzimidide-ether (Lossen, A. 265, 138). Oil. Decomposed by conc. $HClAq$ into $EtCl$ and benzanilide.

PHENYL BENZOATE v. *Benzoyl derivative of PHENOL*.

PHENYL-BENZOIC ACID v. *DIPHENYL-CARBOXYLIC ACID*.

PHENYL-BENZOPHENONE $C_{15}H_{10}O$ i.e. $[1:4] C_6H_5.C_6H_4.CO.C_6H_5$. [104°]. V.D. 9.0. Formed by oxidation of *p*-benzyl-diphenyl with chromic acid (Goldschmidt, M. 2, 487; Köller, M. 12, 501). Formed also from diphenyl, $BzCl$, and $AlCl_3$ (Wolf, B. 14, 2082). Scales, sol. alcohol. Yields benzophenone-*p*-carboxylic acid on further oxidation by CrO_3 .

Oxim. [194°]. Needles. When HCl is passed into its solution in $HOAc$ containing As_2O_3 and the mixture heated in sealed tubes at 100°, it is converted into the isomeric $C_6H_5.C_6H_4.CO.NHOH$ [224°]. The oxim is reduced by sodium-amalgam to the corresponding amine $C_6H_5.C_6H_4.CH(NH_2).C_6H_5$ [77°].

Benzoyl derivative of the Oxim [198°]. Needles (from alcohol).

Phenyl-hydrazide. [144°]. Yellow needles (from dilute alcohol).

Di-phenyl-benzophenone $(C_6H_5.C_6H_4.CO)_2$. [229°]. Formed by the action of $COCl_2$ on diphenyl in presence of $AlCl_3$ (Adam, Bl. [2] 47, 689; A. Oh. [6] 15, 269). Got also by oxidising $CH_2(C_6H_5)_2$ (Weiler, B. 7, 1138). White needles, sol. acetone, v. al. sol. alcohol. Not attacked by fuming HNO_3 , or by H_2SO_4 and HNO_3 at 100°. By adding Na to its solution in alcohol-benzene it is reduced to $(C_6H_5.C_6H_4).CH.OH$. [151°]. S. (alcohol) 1-25 at 15°. Potash-fusion gives diphenyl-*p*-carboxylic acid [218°].

PHENYL-BENZOPHENONE CARBOXYLIC ACID $C_{16}H_{10}Ph.OO.C_6H_4.CO_2H$. [220°]. Formed from diphenyl, phthalic anhydride, and $AlCl_3$ (Kaiser, A. 267, 96). Needles. Yields an oxim.

PHENYL-BENZOYL IS BENZOPHENONE.

PHENYL-BENZOYL-ACETIC ACID $CHBzPh.CO.H$. *Methyl ether* MeA'. Formed from de-oxybenzoic, $NaOEt$, and $ClCO_2H$ (Battner, B. 21, 1316). Oil, decomposed by distillation into $C_6H_5Ph.CO_2H$ and $HOBA$.

PHENYL-BENZOYL-BUTYRIC ACID $CHBzPh.CH_2.CH_2.CO.H$. (*β*-Benzyl-propionic acid. [186°]. Formed from deoxybenzoic, $NaOEt$, and *β*-iodo-propionic ether (Knoevenagel, B. 21, 1344). Needles. Yields MeA' [64 and EtA' [34°].

The isomeric acid $CHBzPh.CHMe.CO_2H$, [215°], formed from *β*-bromo-propionic acid, less sol. alcohol and ether.

PHENYL-BENZOYL-CARBINOL v. *Benzoyl-BENZYL-PROPIONIC ACID* $CHBzPh.CH_2.CO_2H$. [156°]. Formed from deoxybenzoic, $NaOEt$, and chloro-acetic eth (Meyer & Oelkers, B. 21, 1295; Knoevenagel, B. 21, 1344). Small tables (from alcohol).

Di-phenyl-benzyl-propionic acid $CHBzPh.CPh.CO_2H$. [183°]. Got by the action of alcoholic potash on the lactone of oxy-tri-phenyl crotonic acid (Japp & Klingemann, B. 22, 2882). Yields a phenyl-hydrazide $C_{24}H_{18}N_2O$ [185°] and an oxim $C_{24}H_{18}NO$ [152°].

PHENYL-BENZYL ALCOHOL $C_{13}H_{12}O$ i.e. $C_6H_5Ph.CH_2.OH$. Got from $C_6H_5Ph.CH_2$ by treatment with Br and alcoholic potash; the resultant syrupy $C_6H_5Ph.CH_2.OEt$ being treated with H (Adam, Bl. [2] 49, 97). Syrup.

PHENYL-BENZYL-AMIDO-DI-PHENYL METHANE $C_{24}H_{18}N$ i.e. $CHPh.C_6H_4.NPh.C_6H_5$. Formed by heating $NPh.H$ (1 mol.) with benzyl chloride (2 mols.) and $ZnCl_2$ at 210° (Meldola, C. J. 41, 200). Solid; v. sol. ether, insol. alcohol and $HOAc$.

PHENYL-BENZYL-AMINE v. *BENZYL-ANILINE*.

Nitrosamine $C_6H_5NPh.NO$. [58°]. Needles (Antrick, A. 227, 8360). Yields benzyl-aniline and benzylidene-aniline on treatment with alcoholic HCl (O. Fischer, A. 241, 328).

Phenyl-di-benzyl-amine v. *DI-BENZYL-ANILINE*.

Di-phenyl-benzyl-amine $NPh.C_6H_5Ph$. [87°]. Got from $C_6H_5.CSNPh$, zinc-dust, and $HClAq$ (Bernthsen & Trompeter, B. 11, 1761; cf. Wilm & Girard, B. 8, 1196). Needles, al. sol. cold alcohol. Yields a green dye on heating with $HClAq$ and arsenic acid (Meldola, B. 14, 1385).

DI-PHENYL-DI-BENZYL-TETRAZONE $NPh(CH_2Ph).N.N.NPh(CH_2Ph)$. [109°]. Formed from (a)-phenyl-benzyl-hydrazine, $CHCl_3$, and HgO (Michaelis & Phillips, A. 252, 290). Needles.

PHENYL-BENZYL-CARBINOL $C_{13}H_{12}O$ i.e. $CHPh.CH(OH).C_6H_5$. *Toluylene hydrate*. [49°]. Formed by reducing deoxybenzoic, and by the action of alcoholic potash on the same body (Limpricht & Schwanert, A. 155, 63; Goldenberg, A. 174, 332; Zagoumeny, A. 184, 162; Anschütz, A. 261, 298). Formed also [33°] by the action of nitrous acid on $CHPh.CH_2.NH_2$ (Leuckart, B. 22, 1410). Long slender needles (from alcohol), insol. water. Reduced by H_2 to dibenzyl. Yields a liquid acetyl derivative.

PHENYL-BENZYL-ETHER v. *Phenyl ether of BENZYL ALCOHOL*.

PHENYL-BUTANE TRICARBOXYLIC ACID.

acetophenone ether, with aniline (Hofmann, *B.* 250; Leuckhart, *J. pr.* [2] 51, 37). Formed also by the action of phenyl cyanate on phenyl-urea (Kühn a. Henschel, *B.* 21, 504). Needles.

o-Di-phenyl-bisuret $\text{NH}_2\text{CO.NPh.CO.NHPh}$. [165°]. Got from di-phenyl dicyanate and alcoholic NH_3 (Hofmann). Prisms, sol. alcohol.

s-Tri-phenyl-bisuret NPh.CO.NHPh . [148°]. Formed from di-phenyl dicyanate and aniline (H.) and by heating phenyl cyanate with di-phenyl-urea at 150°. Prisms (from alcohol). An isomeride [105°] was got by Schiff (*B.* 3, 651) by distilling phenyl-carbamoyl ether.

References.—Di-BROMO-DI- and OXY-PHENYL-BISURET.

PHENYL-BORATE $\text{C}_6\text{H}_5\text{BO}_2$. Formed by heating phenol (3 pts.) with B_2O_3 (2 pts.), or, better, by heating tri-phenyl borate with alcohol at 150° (Schiff, *A. Suppl.* 5, 202). Sticky mass.

Tri-phenyl borate $(\text{C}_6\text{H}_5)_3\text{B.O}_2$. Formed by boiling phenol with B_2O_3 . Glassy mass, decomposed by hot water.

Tetra-phenyl diborate $(\text{C}_6\text{H}_5)_4\text{B}_2\text{O}_7$. S.G. 1.124. Formed, with the preceding body, by heating $\text{C}_6\text{H}_5\text{BO}_2$ at 350°. Thick oil, quickly decomposed by water.

Phenyl-boric acid $\text{C}_6\text{H}_5\text{B(OH)}_2$. [204°]. Formed from $\text{C}_6\text{H}_5\text{BCl}_2$ and water (Michaelis a. Becker, *B.* 15, 181). Needles, sol. alcohol, ether, and hot water. Powerful antiseptic, with but slight physiological action. With HgCl_2 it gives a pp. of PhHgCl . Reduces ammoniacal AgNO_3 , forming a mirror. On heating, it yields the oxide $\text{C}_6\text{H}_5\text{BO}$ [190°] (above 360°), which forms crystals, sol. alcohol.

Salts.— NaA'' : dimetric tables.— $\text{CaH}_2\text{A}''$: crystals.— AgHA'' : yellow pp.

Ethyl ether Et.A'' (176°). Oil.

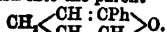
Chloride *v. vol.* i. p. 531.

PHENYL BROMIDE *v.* Bromo-benzene.

PHENYL BROMO-ALLYL OXIDE *v.* Bromo-allyl derivative of Phynol.

PHENYL BROMO-BENZYL KETONE $\text{C}_6\text{H}_5\text{CO.CHBrPh}$. [55°]. Got by brominating phenyl benzyl ketone (Knoevenagel, *B.* 21, 1555).

PHENYL BROMO-BUTYL KETONE $\text{C}_6\text{H}_5\text{CO.CH}_2\text{CH}_2\text{CH}_2\text{Br}$. [61°]. Formed from phenyl oxy-butyl ketone anhydride or its carboxylic acid and conc. HBrAq (W. H. Perkin, jun., *C. J.* 51, 732; *B.* 19, 2559). Six-sided plates, *v.* sol. alcohol. Converted by warm alcoholic potash into the parent



Phenyl di-bromo-butyl ketone $\text{C}_6\text{H}_5\text{CO.CH}_2\text{CHBrCH}_2\text{Br}$. Formed from allyl-acetophenone and Br (Perkin, *C. J.* 45, 188). Oil. Bromine yields $\text{C}_6\text{H}_5\text{Br}_2\text{O}$ [122°] crystallising from dilute alcohol in prisms.

PHENYL BROMO-ETHYL KETONE $\text{C}_6\text{H}_5\text{CO.C}_2\text{H}_4\text{Br}$. Formed from phenyl ethyl ketone and Br in CS_2 (Pampel a. Schmidt, *B.* 19, 2397). Oil with pungent odour.

PHENYL BROMO-ETHYL OXIDE *v.* Bromo-ethyl derivative of Phynol.

PHENYL BROMO-ETHYL SULPHONE $\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{CH}_2\text{Br}$. [50°]. Formed by boiling an aqueous solution of the Na salt of the acid $\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{CH}_2\text{COOH}$ [184°], which is got by bromination of $\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{CH}_2\text{COH}$ (Otto, *pr.* [2] 40, 550). Rectangular tables.

PHENYL BROMO-IMESATIN *v.* IMATIN.

PHENYL-BROMO-METHENYL-DI-ETHYL-TRI-SULPHONE $\text{C}_6\text{H}_5\text{SO}_2\text{CBr(SO}_2\text{CH}_2\text{CH}_3)_3$. [135°]. Formed by bromination of the sulphone $\text{CH(SO}_2\text{Ph)(SO}_2\text{Et)}_3$ (Laves, *B.* 25, 384). Plates (from alcohol) or needles (from Ag).

TRI-PHENYL-BROMO-METHENYL TRI-SULPHONE $\text{CBr(SO}_2\text{Ph)}_3$. [355°]. Got by brominating $\text{CH(SO}_2\text{Ph)}_3$ (Laves, *B.* 25, 351). Amorphous insoluble pp.

PHENYL BROMO-METHYL KETONE *v.* *o*-BROMO-ACETOPHENONE.

PHENYL BROMO-METHYL SULPHONE $\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{Br}$. [48°]. Formed, together with $\text{C}_6\text{H}_5\text{SO}_2\text{CHBr}_2$, [75°], from $\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{COH}$ and Br (Otto, *pr.* [2] 40, 542). Both compounds form monoclinic tables, *v.* sol. hot alcohol.

PHENYL BROMO-(*a*)-NAPHTHYL KETONE $\text{C}_6\text{H}_5\text{CO.C}_{10}\text{H}_7\text{Br}$. [98°]. Formed by bromination of phenyl (*a*)-naphthyl ketone (Elbs a. Steinike, *B.* 19, 1966). Yields a crystalline dinitro-derivative decomposing at about 90°. Yields $\text{C}_6\text{H}_5\text{Br(SO}_2\text{H)}$ [116°] on sulphonation.

PHENYL-BROMO-NITRO-METHANE *v.* BROMO-NITRO-TOLUENE.

PHENYL-BROMO-DI-NITRO-PHENYL-AMINE *v.* BROMO-DI-NITRO-DI-PHENYL-AMINE.

PHENYL-BROMO-NITRO-PHENYL-HYDRAZINE $\text{C}_6\text{H}_5\text{N}_2\text{H.C}_6\text{H}_4\text{Br(NO}_2)$. [3:1:4]. [165°]. Formed from phenyl-hydrazine and $\text{C}_6\text{H}_5\text{Br(NO}_2)_2$ (Willgerodt, *J. pr.* [2] 87, 458). Red needles (from alcohol).

PHENYL-*p*-BROMO-PHENYL-HYDRAZINE $\text{C}_6\text{H}_5\text{N}_2\text{H.C}_6\text{H}_4\text{Br}$. [115°]. Formed by reduction of $\text{C}_6\text{H}_5\text{N}_2\text{C}_6\text{H}_4\text{Br}$ by alcoholic ammoniac sulphide (Janovsky, *B.* 20, 364). Tables.

PHENYL BROMO-PHENYL KETONE *v.* BROMO-BENZOPHENONE.

DI-PHENYL BROMO-PROPYLENE DISULPHONE $\text{C}_6\text{H}_5\text{Br(SO}_2\text{Ph)}_2$. [160°]. Got from $\text{CH}_2\text{Br.CHBrCH}_2\text{Br}$ and NaSPh in alcohol (Stuffer, *B.* 23, 1411). Needles.

PHENYL BROMO-PROPYL KETONE $\text{C}_6\text{H}_5\text{CO.CH}_2\text{CH}_2\text{CH}_2\text{Br}$. [39°]. Formed from 'benzoyl-trimethylene carboxylic' acid and fuming HBr (W. H. Perkin, jun., *C. J.* 47, 844). Crystalline mass, *v.* sol. alcohol.

PHENYL-BUTANE *v.* BUTYL-BENZENE.

Di-phenyl-butane $\text{CHPh.CH}_2\text{CH}_2\text{CH}_2\text{Ph}$. [52°]. Formed by heating di-phenyl-butylene with HI and P at 250° (Freund a. Immerwahr, *B.* 23, 2858). Crystals, *v.* sol. alcohol.

Di-phenyl-butane CHMePh.CHMePh . [123-5°]. Formed by the action of zinc-dust or Na on CHMePhBr (Radziszewski, *B.* 7, 142; Engler, *B.* 7, 1127). Needles (from ether).

Di-phenyl-butane CPh.MeEt . [128°]. Formed from CPh.Me.CO.OH , phosphorus, and HI (Zincke a. Thörner, *B.* 11, 1990). Tables or prisms, *m.* sol. alcohol.

Diphenyl-butane $\text{CH}_2\text{CH(CHPh)}_2$. [300°]. Formed by heating acetophenone with HIAq and P at 180° (Graebe, *B.* 7, 1827). Oil.

References.—AMIDO-, TRI-CHLORO-, and TRI-CHLORO-DI-NITRO- and OXY-PHENYL-BUTANES.

PHENYL-BUTANE TRICARBOXYLIC ACID.

Ethyl ether $\text{C}_6\text{H}_5\text{CH}_2\text{C(COOEt)}_3$. S.G. 1.1008. *m.* 14850 at 20° (388° cor.). Formed from sodium-propane tri-carboxylic ether and benzyl chloride (Bischhoff a. Minz,

PHENYL-BUTYL-THIOALDEHYDE

DI-PHENYL-ISOBUTYL-QUINOXALINE

$C_{16}H_{14}N_2$ i.e. $C_6H_5.NH > C_6H_5.Pr$. [243°].

Formed from benzil, isovaleric aldehyde, and NH_4Aq (Japp & Wynne, *C. J.* 49, 468).— $B^*H.EtCl$: crystalline.

PHENYL-ISOBUTYL-HYDRAZINE

$C_9H_{11}N_2$, $(240^\circ-245^\circ)$. Formed from isobutyl bromide and sodium phenyl-hydrazine (Michaelis & Philips, *B.* 20, 2485; *A.* 252, 282; 270, 122). Liquid, which reduces hot Fehling's solution. Converted by thiophenyl-aniline into oily $C_9H_{11}N_2.SO-B^*H_2SO_4$: plates.

Acetyl derivative $C_9H_{11}N_2.NHAc$. [114°].

PHENYL-BUTYL KETONE $C_9H_{10}O$

Mol. w. 162. (237°) at 720 mm. Got by boiling propyl-benzoyl-acetic ether with alcoholic potash (Pekkin & Calman, *C. J.* 49, 162). Oil.

Phenyl isobutyl ketone $C_9H_{10}O$. Formed from isopropyl-benzoyl-acetic ether (P. & C.) and also by distilling a mixture of calcium benzoate and calcium isovalerate (Popoff, *A.* 162, 153). Liquid. Does not combine with $NaHSO_4$. Yields benzoic, isobutyric, and acetic acids on oxidation.

PHENYL-BUTYL KETONE CARBOXYLIC ACID $C_9H_8O_3$. $CH_3.CO.CH_2.CO_2H$. Ethyl-benzoyl-propionic acid. [38°]. Formed by heating the dicarboxylic acid. Small needles.— CaA' , aq.

Ethyl ether EtA' . Oil.

Phenyl butyl ketone carboxylic ether $C_9H_8O_3$. $CH_3.CO.CH_2.Pr.CO_2Et$. Propyl-benzoyl-acetic acid (251° at 300 mm.). Formed from benzoyl-acetic ether, $NaOEt$, and PrI at 100° (Perkin & Calman, *C. J.* 49, 160). Liquid.

Phenyl isobutyl ketone carboxylic ether $C_9H_8O_3$. $CH_3.CO.CH_2.Pr.CO_2Et$. (237° at 225 mm.). Formed in like manner, using isopropyl iodide.

Phenyl butyl ketone dicarboxylic acid $C_9H_8O_5$. $CH_3.CO.CH_2.CE_2(CO_2H)_2$. Benzoyl-ethyl-isosuccinic ether. Got by saponifying its ether, which is formed from sodium-malonic ether and ω -bromo-acetophenone (Dittlich & Paal, *B.* 21, 3453). Crystalline mass.— $(NH_4)_2A''$: amorphous.— K_2A'' : pearly plates, v. sol. water.— CaA'' aq.— AgA'' : plates. Hydrazine salt. [103°].

Phenyl hydrazide $C_9H_8O_4$. [132°].

PHENYL-BUTYL METHYLENE DIKETONE $C_9H_8O_4$. $CH_3.CO.CH_2.CO.CH_3$. Valeryl-acetophenone. (184° at 30 mm.). Oil. Got from acetophenone, isovaleric ether, and $NaOEt$ (Stylos, *B.* 20, 2181).

PHENYL-BUTYL METHYL KETONE CARBOXYLIC ETHER

$CH_3.CO.OEt(CH_2Ph).CO_2Et$. (c. 297°). Formed from sodium benzyl-acetoacetate and EtI (Conrad, *B.* 11, 1087).

PHENYL-BUTYL OXIDE v. Butyl derivative of Phenol.

PHENYL-ISOBUTYL-PHENYL-THIO-UREA $C_{15}H_{13}N_2S$. $C_6H_5.NH.CO.NH.C_6H_5$. [152°]. Formed from $C_6H_5(NH_2).CH_2.Pr$ and phenyl-thiocarbimide (Mann, *B.* 16, 2023). Plates, sol. alcohol.

DI-PHENYL-ISOBUTYL-QUINOXALINE

$C_{16}H_{14}N_2$ i.e. $C_6H_5.NH < C_6H_5.Pr$. [144°]. Formed from benzil and isobutylphenylene-diamine (Gölzer, *B.* 20, 3257). Needles, v. sol. alcohol.— B^*HCl .

PHENYL-BUTYL-THIO-ALLOPHANIC ACID $NHPh.CO.N(CH_2Ph).ON$. [189°]. Formed from sodium cyanamide, phenyl thiocarbimide, and

isobutyl iodide (Hecht, *B.* 23, 323). Slender needles, v. sl. sol. hot water.

DI-PHENYL-ISOBUTYL-THIO-SEMI-CARBAZIDE $NHPh.CO.NH.NHPh$

Formed from phenylisobutyl-hydrazine and phenyl-thiocarbimide (Michaelis & Philips, *A.* 252, 284). White crystals.

PHENYL-ISOBUTYL-THIO-UREA

$NHPh.CO.NHCO_2H$. [82°]. Formed from phenyl-thiocarbimide and isobutylamine (Hecht, *B.* 23, 315). Needles, m. sol. hot water.

PHENYL-BUTYL-THIOHYDANTOIN

$C_{15}H_{13}NO$. $NH.CO(CH_2Ph)_2$. [179° uncor.]. Formed by fusing phenylthiocarbimide with leucine (Aschan, *B.* 17, 426). Minute colourless prisms.

PHENYL-BUTYRIC ACID $C_{10}H_{12}O_2$ i.e. $CH_3.CH_2.CH_2Ph.CO_2H$. [42°]. (273°). Formed by saponifying the nitrile which is made by the action of EtI and solid $NaOH$ on benzyl cyanide (Neure, *A.* 250, 153). Crystalline mass.— CaA' , 2aq; groups of needles.— AgA' .

Methyl ether MeA' . (228°).

Nitrile $PhOEt.ON$. (245°).

γ -Phenyl- n -butyric acid

$CH_3.Ph.CH_2.CO_2H$. [47.5°]. (290°). Formed from oxy-phenyl-butyric acid and Ml (Burker, *A. Ch.* [6] 26, 459) and from phenyl-isocrotonic acid by protracted treatment with sodium-amalgam (Jayne, *A.* 216, 107). Long flat plates (from water).— CaA' : amorphous mass.

Phenyl-isobutyric acid $CH_3.Ph.CHMe.CO_2H$. Benzyl-methyl-acetic acid. [37°]. (272°). S. 81 at 15°.

Formation.—1. By heating benzyl-methyl-malonic acid (Conrad, *B.* 13, 593).—2. By heating benzyl-methyl-acetoacetic ether with conc. $KOHAq$.—3. By reduction of the phenyl-crotonic acid obtained from benzoic aldehyde, sodium propionate, and propionic anhydride.—4. By reducing phenyl-angelic (methyl-cinnamic) acid with sodium-amalgam (von Miller, *B.* 23, 1888).

Properties.—Plates. Converted by H_2SO_4 at 150° into oxy-methyl-indonaphthene.

Salt.— AgA' . S. 248 at 20°.

Ethyl ether EtA' . (287°). S.G. $\frac{1}{4}$ 1.05.

Oil (Conrad & Bischoff, *A.* 204, 1177). Benzyl ether C_6H_5A' . (320°-325°). S.G. $\frac{1}{4}$ 1.046. A product of the action of sodium on benzyl propionate (Conrad & Hodgkinson, *A.* 193, 312).

Amide $CH_3.Ph.CHMe.CONH_2$. [109°].

Formed by heating the NH_2 salt (Edelmann, *B.* 20, 618). Needles, v. sol. alcohol and ether.

Di-phenyl-butyric acid

$CH_3.Ph.CMePh.CO_2H$. [126°]. Got from its nitrile, which is obtained from α -phenyl-propionitrile and benzyl chloride (Janssen, *A.* 250, 187). Needles, v. sol. ether and alcohol.— NaA' 7aq: long thin needles.— CaA' .— BaA' .— CuA' . [78°].— AgA' : white insoluble powder. Nitrile $C_6H_5.H_2C.ON$. (337°). Oil.

Isomeride v. Di-benzyl-acetic acid.

References.—Bromo-Nitro-Nitro-Amide, and Oxy-phenyl-butyric acid.

PHENYL-ISOBUTYRIC ALDEHYDE

$CH_3.CH(CH_2Ph).CHO$. (327°). Formed by distilling the corresponding lime salt with calcium formate (Miller & Rohde, *B.* 23, 1080). Oil.

PHENYL-BUTYRIC-CARBOXYLIC ACID.

γ-PHENYL-BUTYRIC-*o*-CARBOXYLIC ACID
 $C_6H_5O_2$, i.e. $C_6H_5(CO_2H)CH_2CH_2CH_2CO_2H$.
 [185°]. Formed by heating at 180°-190° the double-lactone of benzoyl-propionic-*o*-carboxylic acid: $C_6H_5\langle CO-O \rangle C \langle O-CO \rangle CH_2$ with HI and P (Roser, B. 18, 8118). Small plates. V. sol. alcohol, sl. sol. cold water.—A"Ba: very soluble in water.

PHENYL-BUTYRO-LACTONE v. *Lactone* of OXYPHENYL-BUTYRIC ACID.

PHENYL-CACODYL v. vol. i. p. 320.

PHENYL-CAMPHORAMIC ACID v. CAMPHORIC ACID.

PHENYL-CAMPEYL-THIO-UREA v. CAMPEYL-THIO-UREA.

PHENYL-CARBAMATE $NHPh.CO_2Ph$. [148°]. Formed by the action, in ethereal solution, of NH_3 on $ClCO_2Ph$ or of NH_4COCl on phenol (Kempt, B. 2, 740; Gattermann, *g.* 244, 48). Formed also, together with $Et.CO_2$, by heating phenyl ethyl carbonate at 800° (Bender, B. 19, 2268). Needles (from water), sol. alcohol and ether. Decomposed by $NaOH$ aq into NH_3 , phenol and $Na.CO_2$. NH_4 aq at 150° forms phenol and urea.

PHENYL-CARBAMIC ACID $NHPh.CO_2H$. *Carbanilic acid*. The ethers of this acid are got by the action of aniline on the chloroformic ethers $Cl.CO_2OR$, and also by the action of phenyl cyanate on alcohols. They are decomposed by potash into CO_2 , aniline, and alcohols.

Acetyl derivative $NPhAc.CO_2H$. The Na salt is formed by passing CO_2 over sodium acetanilide in the cold (Seifert, B. 18, 1858). It is decomposed by water into acetanilide and $NaHCO_3$. By heating at 140° under pressure it is converted into $NPhH.CO_2CH_3.CO_2Na$.

Methyl ether $NHPh.CO_2OMe$. [47°] (Hentschel, B. 18, 978). Prisms. Converted by HNO_3 (S.G. 1.48) into $C_6H_5(NO_2).NH.CO_2Me$ [127°] and $[8:4:2:1]C_6H_5(NO_2).NH.CO_2Me$ [192°] (Van Romburgh, R. T. C. 10, 185). H_2SO_4 forms $SO_3.H_2C_6H_5.NH.CO_2Me$ which is converted by bromine into $C_6H_5Br.NH.CO_2Me$ [98.5°] (Hentschel, *J. pr.* [2] 34, 423). Distillation with lime at 260° gives aniline, methyl-aniline, di-methyl-aniline, and di-phenyl-urea (Nöling, B. 21, 8154).

Ethyl ether $NHPh.CO_2Et$. [52°]. (238°) (Wilm a. Wischin, C. J. 21, 192). Formed as above and also by boiling the product of the action of phenyl-urea on aceto-acetic ether with conc. HCl (Behrend, A. 233, 6) and by the action of sodium acetanilide on chloro-formic ether (Paal a. Otten, B. 23, 2590). Needles (from water). Not affected by boiling conc. HCl aq, but decomposed by HCl aq at 150° into CO_2 , aniline, and $EtCl$. Boiling alcoholic KOH gives aniline and K_2CO_3 . Yields a bromo-derivative [81°], a di-nitro-derivative [110°], and a tri-nitro-derivative [144°]. When distilled with $NaOPh$ at 220° it gives phenol and diphenyl-urea [235°] (Hentschel, *J. pr.* [2] 27, 438). — $NKPh.CO_2Et$. Formed by dissolving phenyl-carbamic ether in alcoholic potash. Hygroscopic needles, decomposed by water.

Chloro-ethyl ether
 $NHPh.CO_2CH_2CH_2Cl$. [51°]. Formed from aniline and $Cl.CO_2OCH_2CH_2Cl$ (Nemirowsky, *J. pr.* [3] 81, 174; Otto, *J. pr.* [2] 44, 15). Needles, sl. sol. hot water. When boiled alone and after-

wards with conc. KOH it yields $NPh\langle CH_2 \rangle CH_2$, [124°], which is converted by HCl aq at 170° into chloro-ethyl-aniline.

Ethylene ether C_6H_5A' . [158°]. Formed from ethylene glycol and phenyl cyanate (Snape, B. 18, 2430; C. J. 47, 783). Prisms.

Propyl ether PrA' . [59°]. Slender needles, v. sol. alcohol (Römer, B. 6, 1101).

Isopropyl ether PrA' . [90°] (Gumpert, *J. pr.* [2] 31, 119; 32, 278); [48°] (Spica, G. 17, 165). Needles (from dilute alcohol).

Di-chloro-propyl ether (Otto, *J. pr.* [2] 44, 22) $CH_2Cl.CHCl.CH_2A'$. [74°]. Prisms.

Isobutyl ether C_6H_5A' . [84°]. (216°). Needles, v. sol. alcohol (Mylus, B. 5, 972).

Heptyl ether C_6H_5A' . [85°]. Formed by the action of phenyl cyanate on the heptyl alcohol got by reducing suberone (Markownikoff, C. B. 110, 466). Prisms (from alcohol).

Glyceryl ether v. GLYCERYL-TRI-PHENYL-CARBAMATE.

Phenyl ether $NHPh.CO_2Ph$. [126°]. Formed from phenyl cyanate and phenol (Gumpert; cf. Hofmann, B. 4, 249). Needles (from benzene). With NH_4 aq it forms phenyl-urea.

Phenylene ethers. The *o* [185°], *m* [164°], and *p* [207°] compounds are got by heating pyrocatechin, resorcin, and hydroquinone respectively with phenyl cyanate (Snape, B. 18, 2428).

Phenylphenyl ether $C_6H_5.C_6H_5A'$. [110°]. Formed from *p*-amido-diphenyl and $ClCO_2Et$ (Zimmermann, B. 18, 1965).

(*α*)-*Naphthyl ether* $C_{10}H_7A'$. [178.5°]. Slender needles (Leuchart a. Schmidt, B. 18, 2340; Snape, C. J. 47, 776). Decomposed by heat into (*α*)-naphthol and phenyl cyanate.

(*β*)-*Naphthyl ether* $C_{10}H_7A'$. [230°]. (L. a. S.); [155°] (S.). Thick prisms. The tetrahydride $C_{10}H_8.CONPhH$ [98.5°] is formed from (*β*)-naphthol ac-tetrahydride and phenyl cyanate.

Di-phenyl-carbamic acid.

Chloride $NPh_2.COCl$. [85°]. Formed from $COCl_2$ and diphenylamine in $CHCl_3$ (Michler, B. 9, 396). White scales (from alcohol).

Ethyl ether $NPh_2.CO_2Et$. [72°]. (above 360°). Formed by heating diphenylamine with $ClCO_2Et$ (Merz a. Werth, B. 6, 1511; Hager, B. 18, 2573). Large prisms (from benzene).

Phenyl ether PhA' . [104°]. Formed from the chloride and $KOPh$ (Lellmann a. Bonhöffer, B. 20, 2122). The compound $C_6H_5(NH_2)A'$ [114°], made in like manner from *o*-nitrophenol, may be reduced to $C_6H_5(NH_2)A'$ [191°]. The *m*- and *p*-nitro-phenyl ethers [90°] and [116°] yield *m*- and *p*-amido-phenyl ethers [183°] and [146°] (Lellmann a. Benz, B. 24, 2111).

• *p*-*Tolyl-ether* C_6H_4A' . [81°]. (L. a. B.).

References.—AMIDO-, BROMO-, DI-BROMO-NITRO-, NITRO-, NITRO-AMIDO-, NITRO-ORTO-, OXY-, OXY-AMIDO-, and NITRO-PHENYL-CARBAMIC ACID and ETHER.

PHENYL-CARBAMINE $C_6H_5.NH_2$. Mol. w. 103. [167°]. S.V. 121.6 (Lossen, A. 254, 78). Formed by distilling aniline with chloroform and alcoholic potash (Hofmann, A. 184, 117). Stinking liquid, quickly decomposed by acids into aniline and formic acid. Changes into the isomeric benzonitrile by heating at 210° (Weith, B. 6, 210). Yields phenyl-thiocarbamide

DI-PHENYL-CARBINOL.

on heating with sulphur. Mixed with propionitrile and ether, it yields, by successive treatment with sodium and water, the compound $\text{C}_6\text{H}_5(\text{NH})\text{CHMe}.\text{CN}$ [97°] (Von Meyer, *J. pr.* [2] 89, 189).

Chloride $\text{NPh}.\text{COCl}$ (212°). Formed from phenyl-thiocarbamide and Cl (Sell a. Zierold, *B. 7*, 1228). Pungent liquid, with nasty smell, yielding *s*-di-phenyl-urea when heated with water at 100°.

PHENYL-CARBAZIC ACID. The crystalline salt $\text{N}_2\text{H}_4.\text{Ph}.\text{CO}.\text{ON}.\text{H}.\text{Ph}$ is formed by the action of CO , on phenyl-hydrazine and water. It is deliquescent, and sl. sol. water and ether (Fischer, *A.* 190, 124).

Methyl ether $\text{NPh}.\text{NH}.\text{CO}.\text{Me}$. [117°]. Short prisms (Heller, *A.* 263, 281).

Ethyl ether $\text{NPh}.\text{NH}.\text{CO}.\text{Et}$. [87°] (F.) [82°] (N.). Formed from phenyl-hydrazine and $\text{ClCO}.\text{Et}$ (E. Fischer, *B.* 22, 1934), or $\text{Ac}(\text{CO}.\text{Et})$ (Nef, *A.* 266, 107). Needles. Ac_2O forms $\text{C}_6\text{H}_5.\text{N}.\text{HAc}.\text{CO}.\text{Et}$ [108°] (H.).

PHENYL-semi-CARBAZIDE $\text{C}_6\text{H}_5.\text{N}_2\text{O}$ *i.s.* $\text{NPh}.\text{NH}.\text{CO}.\text{NH}_2$. [173°]. Formed from potassium cyanate and phenyl-hydrazine hydrochloride (E. Fischer, *A.* 190, 118; Freund, *B.* 21, 2463). Formed also by heating phenyl-hydrazine hydrochloride (1 mol.) with urea (2 mols.) at 160° for 4 hours (Pinner, *B.* 20, 2358; 21, 2329) and by heating di-phenyl-carbazide with urea (Skinner a. Rubemann, *C. J.* 53, 550; *B.* 20, 3378). Prisms, v. sol. hot water. Yields di-oxy-phenyl-triazole [268°] on heating with urea. By heating at 160° it is converted into di-phenyl-urazine $\text{C}_6\text{H}_5.\text{N}_2\text{O}$ [264°] and other products. COCl_2 forms $\text{C}_6\text{H}_5.\text{N}_2\text{O}$ [167°].

Benzoyl derivative $\text{NPh}.\text{Bz}.\text{NH}.\text{CO}.\text{NH}_2$. [203°]. Formed from benzoyl-phenyl-hydrazine cyanate (Michaelis a. Schmidt, *A.* 252, 317).

Di-phenyl-semi-carbaside $\text{C}_6\text{H}_5.\text{NH}.\text{CO}.\text{N}.\text{HPh}$. [173°]. Formed from phenyl-hydrazine by combination with phenyl cyanate; and also by heating phenyl-hydrazine with phenyl-urea (Kühn, *B.* 17, 2888; Skinner, *C. J.* 53, 559). Needles or plates (from alcohol or benzene), sl. sol. water. COCl_2 in benzene forms $\text{C}_6\text{H}_5.\text{N}_2\text{O}$ [173°] (Freund, *B.* 21, 2465).

Di-phenyl-carbaside $\text{CO}(\text{N}.\text{H}.\text{Ph})_2$. [151°] (S. a. K.); [164°] (E. Fischer, *B.* 22, 1930). Formed by heating phenyl-hydrazine (2 mols.) with carbamic ether (1 mol.) (Skinner a. Rubemann, *C. J.* 53, 550; *B.* 20, 3372). Formed also from phenyl-hydrazine and COCl_2 (Heller, *A.* 263, 277). Crystalline. Forms with HgCl_2 a crystalline compound $\text{B}.\text{HgCl}_2$ not melted at 186°. Alcoholic potash forms a red solution containing di-phenyl-carbasone $\text{N}_2\text{H}_4.\text{Ph}.\text{CO}.\text{N}:\text{NPh}$ crystallising in orange needles [157°]. Benzene and CS_2 form $\text{CS} \leftarrow \text{NPh} \leftarrow \text{C}:\text{N}:\text{NPh}$ [170°] (Freund a. Kuh, *B.* 23, 2833).

PHENYL-CARBAMIDE *v.* Phenyl isocyanate, vol. ii. p. 815.

DI-PHENYL-DI-CARBIMIDO-TETRA-P-AMIDO-TETRA-TOLYL-DI-O-SULPHIDE

$\text{Ph}.\text{N}.\text{C} \leftarrow \text{NH}.\text{C}.\text{H}.\text{S}.\text{C}.\text{H}.\text{NH} \leftarrow \text{C}:\text{NPh}$. *Di-thio-p-tolyl-di-phenyl-di-guanidine*. [c. 119°]. Formed by heating di-thiocarbonyl-tetra-amido-tetra-tolyl-di-sulphide with aniline and HgO (Truhlar, *B.* 20, 874). Amorphous; v. sol. alcohol.

DI-PHENYL-CARBINOL $\text{C}_{12}\text{H}_{10}\text{O}$ *i.s.*

$\text{Ph}.\text{CH}(\text{OH})$. *Benzhydrol*. Mol. w. 184. [68°] (298°). S. 0.5 at 20°. *Initial velocity of etherification* 22 (Menschutkin, *J. R.* 1882, 189). Formed by reducing benzophenone with sodium-amalgam (Linnemann, *A.* 188, 6; Beckmann, *B.* 22, 915); or by heating benzophenone with zinc and alcoholic KOH (Zagumenny, *A.* 184, 174). Slender silky needles, v. e. sol. alcohol and ether. Converted into benzophenone by oxidation with chromic acid. Bromine forms a dibromo-benzhydrol [163°]. Zn and HOAc form benzpinacone. Zn and HCl in acetic acid solution reduce it to tetra-phenyl-ethane. Distillation partly resolves benzhydrol into water and benzhydrol ether. P_2S_5 forms $\text{C}_{12}\text{H}_{10}(\text{SH})_2$ [151°] and oily $\text{Ph}.\text{CH}(\text{SH})$ (Engler, *B.* 11, 922).

Ethyl derivative $\text{C}_{12}\text{H}_{12}\text{OEt}$. (288°). S.G. 22 1.03. From benzhydrol, alcohol, and H_2SO_4 , or from $\text{Ph}.\text{CHBr}$ and alcoholic KOH (Friedel a. Balsohn, *Bl.* [2] 33, 389). Liquid.

Isoamyl derivative $\text{C}_{12}\text{H}_{14}\text{OC}_5\text{H}_{11}$. (810°).

Chloride $\text{Ph}.\text{CHCl}$. [14°]. From benzhydrol and HCl (Engler a. Bethge, *B.* 7, 1128).

Bromide $\text{Ph}.\text{CHBr}$. [45°]. From di-phenyl-methane and bromine at 160° (F. a. B.). Water at 150° decomposes it into benzhydrol and benzhydrol ether. Conc. NH_4Aq forms mono- and di-benzhydrol-amine (Friedel a. Balsohn, *Bl.* [2] 33, 587).

Acetyl derivative $\text{Ph}.\text{CH}.\text{OAc}$. [42°] (302°). S.G. 22 1.49. Prisms, v. sol. alcohol, acetic acid, and ether (Vincent, *Bl.* [2] 85, 804).

Benzoyl derivative $\text{Ph}.\text{CH}.\text{OBz}$. [89°]. Non-volatile. Trimetric, *abc* = 1 : 477 : 668.

Succinyl derivative $(\text{Ph}.\text{CH}.\text{O})_2.\text{C}_2\text{H}_2$. [142°]. Gives, on distillation, succinic acid and benzhydrolene $\text{C}_{12}\text{H}_{10}$ [210°].

Anhydride $\text{C}_{12}\text{H}_{10}\text{O}$ *i.s.* $\text{Ph}.\text{C} \leftarrow \text{C}(\text{Ph})_2$ (7)

[111°]. (315°) at 745 mm. From benzhydrol by long boiling with water or by treatment with PCl_5 , BzCl , or diluted H_2SO_4 . Monoclinic crystals (from benzene). Reduced by zinc and HCl in HOAc to tetra-phenyl-methane (Zagumenny, *J. R.* 12, 431). Zincke a. Thörner (*B.* 11, 1398) obtained this anhydride by heating benzpinacone, $\text{C}_{10}\text{H}_{12}\text{O}_2$, and consequently assume the formula $\text{C}_{12}\text{H}_{10}\text{O}$.

References.—Di-AMIDO-, Di-BROMO-, and OXY-DI-PHENYL-CARBINOL.

Tri-phenyl-carbinol $\text{C}_{18}\text{H}_{14}\text{O}$ *i.s.* $\text{CPh}_3.\text{OH}$. Mol. w. 260. [159°] (above 800°).

Formation.—1. By boiling tri-phenyl-methane with chromic acid mixture (Hemilian, *B.* 7, 1203).—2. From $\text{CPh}_3.\text{Br}$ and water.—3. By the action of water on CPh_3I got from AlCl_3 , benzene, and COCl_2 , or $\text{OCl}_2.\text{COCl}$ (Friedel a. Crafts, *A. Ch.* [6] 1, 499; Hentschel, *J. pr.* [2] 86, 811).—4. By heating its dicarboxylic acid with baryta (Hemilian, *B.* 19, 3078).

Properties.—Six-sided plates, v. sol. alcohol. *Acetyl derivative* $\text{CPh}_3.\text{OAc}$. [99°]. Prisms (Allen a. Kölliker, *A.* 227, 116).

Methyl ether $\text{CPh}_3.\text{OMe}$. [82°]. Laminæ.

Ethyl ether $\text{CPh}_3.\text{OEt}$. [79°] (F. a. C.); [83°] (A. a. K.).

Chloride *v.* CHLORO-TRI-PHENYL-METHANE.

DI-PHENYL-CARBINOL CARBOXYLIC ACID.

DI-PHENYL-CARBINOL CARBOXYLIC

ACID v. OXY-BENZYL-BENZOIC ACID.

Di-phenyl-carbinol dicarboxylic acid
 $\text{CPh}(\text{OH})(\text{CO}_2\text{H})_2$. Formed by heating benzil di-o-carboxylic (diphthalic) acid with KOHAq (50 p.c.) at 180° for 5 minutes (Graebe & Juillard, *A.* 242, 238). The acid splits up at the moment of liberation into water and anhydride. — BaA"aq.

Anhydride $\text{C}_{12}\text{H}_8\text{O}_4$. [203°]. S. 022 at 28° . Formed as above, and also by reducing benzophenone di-o-carboxylic acid. Monoclinic crystals (from alcohol). On heating, it yields a white sublimate [172°] reconverted by treatment with NaOHAq and HCl into the original anhydride. Phenyl-hydrazine gives $\text{C}_{12}\text{H}_8\text{N}_2\text{O}_4$, H_2SO_4 and HNO_3 give $\text{C}_{12}\text{H}_8(\text{NO}_2)_2\text{O}_4$ [c. 276°], which forms EtA' [148°]. — Ba($\text{C}_{12}\text{H}_8\text{O}_4$), 2/3 aq. — CuA', 2aq. — AgA'. — $\text{C}_{12}\text{H}_8\text{MeA}'$. [155°]. — EtA'. [100°]. — $\text{C}_{12}\text{H}_8\text{O}_4(\text{NH}_2)_2$. [160°]. Needles.

Isomeride v. OXY-BENZYL-ISOPHTHALIC ACID.

Di-phenyl-carbinol tri-carboxylic acid
 $\text{C}(\text{OH})(\text{CO}_2\text{H})(\text{CO}_2\text{H})_2$. Anhydride $\text{C}_{12}\text{H}_8\text{O}_6$. [170°]. Formed by heating benzil di-o-carboxylic acid with NaOHAq (4 p.c.) at 112° for 8 minutes (G. a. J.). Minute crystals, sl. sol. cold water. Gives off CO_2 on heating, yielding the anhydride of di-phenyl-carbinol dicarboxylic acid.

Ethers of the anhydride MeA". [148°]. — EtA". [108°]. Prisms, v. sol. alcohol.

Tri-phenyl-carbinol o-carboxylic acid
 $\text{CPh}_2(\text{OH})\text{CO}_2\text{H}$. The Na salt is formed by heating di-phenyl-phthalide with NaOHAq, but the acid splits up on liberation into water and its anhydride, di-phenyl-phthalide (Baeyer, *A.* 202, 50).

Tri-phenyl-carbinol m-carboxylic acid. [182°]. Formed by oxidation of di-phenyl-m-tolyl-methane with CrO_3 and HOAc (Hemilian, *B.* 16, 2369). Trimetric plates.

Tri-phenyl-carbinol p-carboxylic acid (?). [187°]. Formed by oxidation of $\text{CHPh}_2\text{C}_6\text{H}_4\text{CHO}$ (Oppenheim, *B.* 19, 2028) or of di-phenyl-tolyl-methane (Hemilian, *B.* 7, 1210). Needles. — BaA', 7aq. Needles, v. sl. sol. cold water.

Tri-phenyl-carbinol dicarboxylic acid. Anhydride $\text{CPh}_2\text{C}(\text{CO}_2\text{H})_2$.

Di-phenyl-phthalide carboxylic acid. [246°]. Formed by oxidation of di-phenyl- η -xylyl-methane, di-phenyl-tolyl-methane o-carboxylic acid, di-phenyl-tolyl-carbinol m-carboxylic acid, or di-phenyl-methyl-phthalides (Hemilian, *B.* 16, 2372). Crystals, v. sol. alcohol and HOAc. Yields benzophenone and terephthalic acid on fusion with potash. Zinc-dust and NaOHAq reduce it to tri-phenyl-methane dicarboxylic acid.

Tri-phenyl-carbinol dicarboxylic acid
 $\text{C}_{12}\text{H}_8\text{O}_4$, i.e. $\text{CPh}_2(\text{OH})\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$. [1:3:4]. [190°]. Formed by oxidation of di-phenyl-xylyl-methane with $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 (Hemilian, *B.* 19, 8072). Needles (from water), v. e. sol. alcohol. On fusion it yields an amorphous anhydride $\text{C}_{12}\text{H}_8\text{O}_4$. On fusion with Ba(OH)₂ it forms tri-phenyl-carbinol. — AgA": pp.

Tri-phenyl-carbinol dicarboxylic acid
 $\text{CPh}_2(\text{OH})\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$. [1:2:4]. Anhydride $\text{C}_{12}\text{H}_8\text{O}_4$. Di-phenyl-phthalide carboxylic acid. [228°]. Formed by oxidation of the correspond-

ing di-phenyl-xylyl-methane (H.). Tables (containing EtOH). — CaA', 3aq. — AgA': needles.

DI-PHENYL-CARBINYLAMINE $\text{C}_{12}\text{H}_{12}\text{N}_2$, i.e. CHPh_2NH_2 . Benzhydrolamine. *Ezo-amido-di-phenyl-methane*. (289°). Formed, together with tetra-phenyl-di-carbinyl-amine, by leaving benzhydrol bromide, CHPh_2Br , with conc. NH_4Aq for 48 hours (Friedel & Balsohn, *Bl.* [2] 83, 587). Got also by reducing benzophenone-oxim in alcoholic solution by sodium-amalgam and acetic acid (Goldschmidt, *B.* 19, 3233).

Properties. — Alkaline liquid, absorbing CO_2 from the air.

Salts. — B'HCl: [270°]; long needles, sl. sol. cold water. — B'H₂PCl₂, 2aq.: lancet-like needles (L. a. B.); B'H₂PCl₂, aq. (G.). — B'H₂CO₃. [91°].

Formyl derivative $\text{Ph}_2\text{CH.NH.CHO}$. [182°]. (860°). Formed, almost quantitatively, by heating benzophenone with ammonium formate at 200° – 220° (Leuchart & Bach, *B.* 19, 2129).

Urea $\text{Ph}_2\text{CH.NH.CO.NH}_2$. [143°] (L. a. B.).

Tetra-phenyl-di-carbinyl-amine $(\text{Ph}_2\text{CH})_2\text{NH}_2$. [136°]. Prepared as above, crystallises from alcohol in slender needles, not affected by MeI or AcCl at 100° (F. a. B.).

Tri-phenyl-carbinyl-amine CPh_2NH_2 . [103°]. Formed by passing dry NH_3 through a solution of CPh_2Br in benzene (Hemilian & Silberstein, *Bl.* [2] 43, 118; *B.* 17, 741; cf. Nauen, *B.* 17, 442). Needles, sl. sol. cold alcohol. Yields B'HCl, B'H₂PCl₂, 7aq. CPh_2NHMe [73°], CPh_2NMe_2 [97°], CPh_2NHPH [145°], $\text{CPh}_2\text{NHCH}_2\text{Ph}$ [110°], and the acetyl derivative CPh_2NHAc [208°]. Forms a crystalline oxalate [253°] (Elbs, *B.* 17, 701), and the compounds $\text{C}_{12}\text{H}_{11}\text{NBr}$, $\text{B}'\text{I}$, and $\text{B}'\text{I}_2$.

PHENYL-CARBINYL CHLORIDE v. CHLORO-TRI-PHENYL-METHANE.

TRI-PHENYL - CARBINYL - MALONIC ETHER $\text{CPh}_2\text{CH}(\text{CO}_2\text{Et})_2$. [233°]. Got from sodium malonate ether and CPh_2Br (Henderson, *B.* 20, 1014). Needles (from alcohol).

TRI-PHENYL-CARBINYL SULPHOCYANIDE CPh_2NCS . [137°]. Formed from CPh_2Br and ammonium sulphocyanide (Elbs, *B.* 17, 700).

TRI - PHENYL - CARBINYL - TOLUIDINE $\text{CPh}_2\text{NHCH}_3$. The o [142°] and p [177°] compounds are formed from CPh_2Br and o and p toluidine respectively (Elbs, *B.* 17, 706). The p-compound yields a crystalline nitrosamine [145°–148°].

PHENYL-CARBIZINE. Formyl derivative $\text{C}_6\text{H}_5\text{N} \begin{smallmatrix} \diagup \text{CO} \\ \diagdown \text{CO} \end{smallmatrix}$. [72°]. (256°). Formed by the action of COCl_2 in benzene on the phenyl-hydrazide of formic aldehyde (Freund, *B.* 21, 1240, 2458). Needles (from CS₂), v. sol. alcohol and ether. Decomposed by boiling Na_2CO_3 into CO_2 and the phenyl-hydrazide of formic aldehyde.

Acetyl derivative $\text{CO} \begin{smallmatrix} \diagup \text{NPh} \\ \diagdown \text{NAc} \end{smallmatrix}$. [94°]. (280°). Formed in like manner from acetic aldehyde. Monoclinic prisms; *abc* = 1:2:10:1:1:567; β = $73^\circ 23'$.

Propionyl derivative. [63°]. Needles. Benzoyl derivative $\text{CO} \begin{smallmatrix} \diagup \text{NPh} \\ \diagdown \text{NPh} \end{smallmatrix}$. [114°].

Needles (from alcohol) or plates (from HOAc).

PHENYL CARBONATES.
 Phenyl-carbonic acid $\text{C}_6\text{H}_5\text{O.CO}_2\text{H}$.

Sodium salt PhO.CO.Na . Prepared by treating dry sodium phenylate in the cold for a month with CO_2 until it has taken up the calculated quantity of the gas. The product is a very hygroscopic powder.

Reactions.—1. With water it gives off half its CO_2 in gaseous form: $2\text{PhO.CO.Na} + \text{H}_2\text{O} = \text{PhONa} + \text{PhOH} + \text{NaHCO}_3 + \text{CO}_2$.—2. At 120° it splits up into CO_2 and PhONa .—3. Heated rapidly to 180° – 200° it gives off smaller quantities of CO_2 together with phenol, the residue being sodium salicylate.—4. In a sealed tube at 120° – 180° for several hours it changes completely to sodium salicylate: $\text{C}_6\text{H}_5\text{O.CO.Na} = \text{C}_6\text{H}_4(\text{OH})\text{CO}_2\text{Na}$ (R. Schmitt, *J. pr.* [2] 31, 408).

Di-phenyl carbonate $\text{C}_6\text{H}_5\text{O}_2$, i.e. $\text{CO}(\text{OPh})_2$, 78° (Kempt, *J. pr.* [2] 1, 404; Hentschel, *J. pr.* [2] 27, 41; 36, 315); [88°] (Richter, *J. pr.* [2] 27, 41). (303°). Formed by passing COCl_2 into an aqueous solution of NaOPh , or into phenol containing AlCl_3 . Formed also from $\text{ClCO}_2\text{CCl}_3$, phenol, and AlCl_3 . Needles (from alcohol). Alcoholic potash forms phenol and K_2CO_3 . NaSEt gives NaSPh and $(\text{EtS})_2\text{CO}$ (Seiffert, *J. pr.* [2] 31, 464).

References.—DI-BROMO- and NITRO-PHENYL CARBONATE.

DIPHENYL o-CARBOXYLIC ACID $\text{C}_{14}\text{H}_{10}\text{O}_3$, i.e. $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2\text{H}$ [1:2]. *Phenyl-benzoic acid*. Mol. w. 198. [111°]. Formed by potash-fusion from diphenylene ketone (Fittig a. Ostermaier, *B.* 5, 993; A. 166, 374; Schmitz, A. 193, 115). Formed also, together with diphenylene ketone oxide, by distilling sodium salicylate with triphenyl phosphate (R. Richter, *J. pr.* [2] 28, 805). Small needles (from hot alcohol), m. sol. hot water.— KA^{aq} .— BA^{aq} .— CA^{aq} .— CA^{aq} .— AG^{aq} .

Ethyl ether EtA^{a} . (300°–305°).

Tetrahydride $\text{C}_{14}\text{H}_{12}\text{O}_3$, i.e. $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2\text{H}$. *Phenyl-hexamethylene carboxylic acid*. [305°]. Formed by heating the corresponding dicarboxylic acid, and by the hydrolysis of phenylhexamethylenyl methyl ketone carboxylic ether (Kipping a. W. H. Perkin, jun., *C.* 57, 319). Rosettes of crystals (from ligroin).— AG^{a} : amorphous pp.

Diphenyl m-carboxylic acid

$\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2\text{H}$. [161°]. Formed by oxidation by chromic acid and HOAc from [1:3] $\text{C}_6\text{H}_4\text{Ph}_2$, from $\text{C}_6\text{H}_4\text{PhMe}$, and from $\text{C}_6\text{H}_4\text{Ph.CH}_2\text{Br}$ (Schmidt a. Schultz, A. 203, 182; Adam, A. *Ch.* [6] 15, 243). It is also a product of the fusion of benzoic acid with potash (Barth a. Schroeder, *M.* 8, 808). Leaflets (from alcohol), sl. sol. water. Yields isophthalic acid on oxidation.— NA^{a} , 2aq.— CA^{a} , 8aq.— BA^{a} , 3aq: needles.— BA^{a} , 4aq.

Ethyl ether EtA^{a} . (above 360°). Oil.

Diphenyl p-carboxylic acid $\text{C}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2\text{H}$, [210°]. Formed by saponification of its nitrile, which is got by heating potassium diphenyl sulphamate with KCO_2 in a current of dry CO_2 (Doebner, A. 172, 109). Formed also by oxidation of [1:3] $\text{C}_6\text{H}_4\text{Ph}_2$ or [1:4] $\text{C}_6\text{H}_4\text{PhMe}$ (Schultz, A. 274, 213; Carnelley, *O. J.* 87, 718). It is also a product of the fusion of benzoic acid with potash. Tufts of needles (from alcohol), r. sl. sol. hot water. May be sublimed. Yields terephthalic acid on oxidation.— BA^{a} .— CA^{a} .

Ethyl ether EtA^{a} . [48°]. Prisms.

Nitrile $\text{C}_{14}\text{H}_9\text{ON}$. [85°]. Crystals.

Anilide $\text{C}_6\text{H}_4\text{CO.NHPh}$. [234°]. Got by heating $\text{C}_6\text{H}_4\text{O}(\text{NOH})\text{C}_6\text{H}_5$ with HOAc , Ac_2O , and dry HCl at 100° (Koller, *M.* 12, 503).

Diphenyl di-o-carboxylic acid $\text{C}_{14}\text{H}_{10}\text{O}_4$, i.e. [2:1] $\text{CO}_2\text{H.C}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2\text{H}$ [1:3]. *Diphenic acid*. Mol. w. 242. [238°]. Formed by the oxidation of phenanthraquinone or phenanthrene (Fittig a. Ostermayer, A. 166, 361; Schmitz, A. 193, 115). It is also produced when phenanthraquinone is boiled with conc. alcoholic potash (Anschütz a. Schultz, A. 196, 50; 203, 97). Plates or prisms, m. sol. hot water. May be sublimed. By exhaustive chlorination with SbCl_5 , it yields perchloro-diphenyl, together with a small quantity of perchloro-benzene (Mers a. Weith, *B.* 16, 2832). Distillation over with red-hot CaO yields diphenylene ketone; distillation with $\text{Ca}(\text{OH})_2$ gives diphenyl.

Salts.— BA^{a} 4aq: v. sol. water.— CA^{a} 2aq.— MA^{a} 4aq.— AG^{a} : bulky white pp.

Methyl ethers MeA^{a} . [73.5°].— MeHA^{a} . [110°]. Plates, m. sol. water. Got by boiling the anhydride with MeOH .

Ethyl ethers EtA^{a} . [42°]. Crystals, insol. Ag (Hummel, A. 193, 128).— EtHA^{a} . [88°].

Anhydride $\text{C}_{14}\text{H}_8\text{O}_4$. [213°].

Formed by boiling the acid with AsCl_3 or As_2O_3 (Anschütz, *B.* 10, 1884; 18, 1802; Graebe, *B.* 20, 848; A. 247, 261). Needles, insol. water, sol. alcohol. Decomposed by heat into CO_2 and diphenylene ketone. H_2SO_4 at 100° forms diphenylene ketone carboxylic acid [217°]. Phenyl-hydrazine forms the crystalline compound $\text{CO}_2\text{H.C}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2\text{N.NHPh}$ [174° cor.] which at 250° yields $\text{C}_{14}\text{H}_8\text{O}_4 > \text{N.NHPh}$ [150°]. Benzene and AlCl_3 form an acid [148°].

Chloride $\text{C}_{14}\text{H}_8\text{O}_4\text{Cl}_2$. [98°]. Formed from the anhydride and PCl_5 . Yields di-ox. phenanthrene on reduction.

Imide $\text{C}_{14}\text{H}_8\text{O}_4\text{N}_2$. [212°]. Formed by warming the imide with conc. NH_4Ag .

Amic acid $\text{C}_{14}\text{H}_8\text{O}_4(\text{CONH})_2$. [193°]. Got by boiling the anhydride with NH_4Ag . Plates (from alcohol). Converted by heat into the imide.

Imide $\text{C}_{14}\text{H}_8\text{O}_4\text{N}_2$. [2202]. Formed as above, and also by the action of conc. HClAg on the mono-oxim of phenanthraquinone (Wegerhoff, A. 252, 18). Needles (from alcohol), sl. sol. hot water. Yields an acetyl derivative [92°], and forms $\text{C}_{14}\text{H}_8\text{O}_4(\text{NMe})_2$, $\text{C}_{14}\text{H}_8\text{O}_4(\text{NMe})$, and $\text{C}_{14}\text{H}_8\text{O}_4(\text{NMe})_2$.

Diphenyl om-dicarboxylic acid

[2:1] $\text{CO}_2\text{H.C}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2\text{H}$ [1:3]. *Isodiphenic acid*. [216°]. Formed by fusing diphenylene ketone carboxylic acid with potash (Fittig a. Lieppmann, *B.* 12, 163; A. 193, 155; 200, 9). Needles (from hot water). Yields diphenylene ketone on heating with lime. Gives isophthalic acid on oxidation with CrO_3 .— BA^{a} 6aq. Crystalline.— CA^{a} 2aq.— AG^{a} : pp., sl. sol. hot water.

Methyl ether MeA^{a} . [69.6°].

Ethyl ether EtA^{a} . Thick oil.

Diphenyl op-di-carboxylic acid

[2:1] $\text{CO}_2\text{H.C}_6\text{H}_4\text{C}_6\text{H}_4\text{CO}_2\text{H}$ [1:4]. [252°]. Formed by saponification of its nitrile [158°] which is got by Sandmeyer's reaction from op-di-amido-diphenyl (Reuland, *B.* 22, 8018).

Diphenyl di-*m*-carboxylic acid. [above 340°]. Formed by the action of nitrous acid on di-*p*-amido-diphenyl dicarboxylic acid (Griess, *B.* 21, 982). Small needles, almost insol. cold water.—**BaA**" 8¼aq; crystalline aggregates.

Diphenyl di-*p*-carboxylic acid [4:1] $\text{C}_6\text{H}_4\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4\text{CO}_2\text{H}$ [1:4]. Formed by saponification of its nitrile, and also by oxidation of *p*-ditolyl (Doebner, *B.* 9, 129, 272; *A.* 172, 109). Amorphous powder, nearly insol. most solvents.—**CaA**"': insoluble pp.—**BaA**"'.—**AgA**"': white pp.

Ethyl ether EtA". [112°]. Prisms.

Nitrile $\text{C}_{12}\text{H}_8(\text{CN})_2$. [234°]. Formed by heating potassium diphenyl disulphate with **KCy**. Needles (from alcohol).

Diphenyl dicarboxylic acid $\text{C}_6\text{H}_4\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_4\text{CO}_2\text{H}$ [1:8:5]. [*c.* 310°]. Formed by heating benzoic aldehyde with $\text{CH}_3\text{COCO}_2\text{H}$ and baryta-water (Doebner, *B.* 23, 2381; 24, 1760). Crystals, v. sl. sol. cold **HAc**. Yields diphenyl on distillation with lime.—**BaA**" 4¼aq; needles.—**CaA**"'.—**CaA**"'.

Diphenyl tricarboxylic acid $\text{C}_6\text{H}_3\text{O}_4$, i.e. $\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3\text{CO}_2\text{H} \cdot \text{C}_6\text{H}_3\text{CO}_2\text{H}$. Formed by fusing diphenylene ketone dicarboxylic acid with **KOH** (Bamberger & Hooker, *B.* 18, 1035; *A.* 229, 166). White crystalline powder, v. sl. alcohol and ether, sl. sol. hot water.—**PbA**"': insoluble crystalline pp.—**AgA**"', white pp.

References.—**AMIDO**-, **BROMO**-, **IODO**-, **NITRO**-, and **OXY**-DIPHENYL and **PHENYL CARBOXYLIC ACIDS**.

PHENYL-CETYL-AMINE v. **CETYL-ANILINE**.
PHENYL-CHELIDAMIC ACID v. **CHELIDONIC ACID**.

PHENYL-CHLORO-ACETIC ACID v. **CHLORO-PHENYL-ACETIC ACID**.

PHENYL CHLORO-BENZYL KETONE $\text{C}_6\text{H}_4\text{CO} \cdot \text{CHCl} \cdot \text{C}_6\text{H}_5$. [65°]. (Curtius, *J. pr.* [2] 44, 547). Formed by reducing phenyl dichloro-benzyl ketone with iron and acetic acid (Lashovitch, *B.* 17, 1163). V. sol. alcohol.

Phenyl di-chloro-benzyl ketone $\text{C}_6\text{H}_4\text{CO} \cdot \text{CCl}_2 \cdot \text{C}_6\text{H}_5$. [71°]. (Zinin, *A.* 119, 177; [61°] (*L.*). Formed from benzil and **PCl**₅. Prisms (from ether). Reduced by zinc and **HCl** to phenyl benzyl ketone.

PHENYL CHLORO-BENZYL SULPHONE $\text{C}_6\text{H}_4\text{CO} \cdot \text{CHCl} \cdot \text{C}_6\text{H}_4\text{SO}_2\text{H}$. Formed by heating benzylidene chloride with $\text{C}_6\text{H}_5\text{SO}_2\text{Na}$ and alcohol at 150° (Otto, *J. pr.* [2] 40, 517). Needles (from **HOAc**), sl. sol. hot alcohol.

PHENYL-CHLORO-ETHANE v. **CHLORO-ETHYL-BENZENE**.

PHENYL CHLORO-ETHYL OXIDE v. **Chloro-ethyl derivative of PHENOL**.

PHENYL CHLORO-ETHYL SULPHONE $\text{C}_6\text{H}_4\text{SO}_2\text{CH}_2\text{CH}_2\text{Cl}$. [56°]. Formed by the action of **PCl**₅ or **HCl** on phenyl oxy-ethyl sulphone (Otto, *J. pr.* [2] 30, 197). Six-sided tablets (from benzene), sl. sol. water.

Reactions.—1. Boiling with alcohol and **AgO** converts it into $\text{C}_6\text{H}_5\text{SO}_2\text{C}_2\text{H}_4\text{OH}$.—2. By heating with $\text{C}_6\text{H}_5\text{SO}_2\text{Na}$ in alcoholic solution it is converted into $(\text{C}_6\text{H}_5\text{SO}_2)_2\text{C}_2\text{H}_4$.—3. **Sodium-amalgam** reduces it, in alcoholic solution, to benzene sulphinic acid.—4. Alcoholic **NaOEt** forms $\text{C}_6\text{H}_5\text{SO}_2\text{C}_2\text{H}_4\text{OEt}$.—5. Converted by heating in sealed tubes with dry **AgO** and benzene into $(\text{C}_6\text{H}_5\text{SO}_2\text{C}_2\text{H}_4)_2\text{O}$.—6. **Ammonia**

forms $(\text{C}_6\text{H}_5\text{SO}_2\text{C}_2\text{H}_4)_2\text{NH}$.—7. Alcoholic **KHS** produces $(\text{C}_6\text{H}_5\text{SO}_2\text{C}_2\text{H}_4)_2\text{S}$. [124°].

Phenyl chloro-ethyl sulphone $\text{C}_6\text{H}_5\text{SO}_2\text{CHClCH}_3$. [52°]. Formed by heating aqueous $\text{CH}_3\text{COCH}_2\text{CO}_2\text{Na}$ (1 mol.) with sodium benzene sulphinate (2 mols.) at 100° (Otto, *J. pr.* [2] 40, 532). Crystals (from alcohol).

PHENYL-CHLORO-IMESAMIN v. **ISATTIN**.

PHENYL CHLORO-METHENYL DI-ETHYL TRI-SULPHONE $\text{CCl}(\text{SO}_2\text{Ph})(\text{SO}_2\text{Et})_2$. [180°]. Got by chlorinating $\text{CH}(\text{SO}_2\text{Ph})(\text{SO}_2\text{Et})_2$ (Laves, *B.* 25, 363). Plates, sl. sol. hot water.

TRI-PHENYL CHLORO-METHENYL TRI-SULPHONE $\text{CCl}(\text{SO}_2\text{Ph})_3$. [260°]. Got by chlorinating $\text{CH}(\text{SO}_2\text{Ph})_3$ (Laves, *B.* 25, 350).

PHENYL CHLORO-METHYL KETONE v. ***o*-CHLORO-ACETOPHENONE**.

PHENYL CHLORO-METHYL SULPHONE $\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{Cl}$. [53°]. Formed by boiling an aqueous solution of $\text{C}_6\text{H}_5\text{SO}_2\text{Na}$ (2 mols.) with $\text{CHCl}_3\text{CO}_2\text{Na}$ (1 mol.), the yield being nearly the theoretical quantity (Otto, *J. pr.* [2] 40, 527; *B.* 21, 556). Formed also from $\text{C}_6\text{H}_5\text{SO}_2\text{Na}$ and CH_2Cl_2 .

Phenyl di-chloro-methyl sulphone $\text{C}_6\text{H}_5\text{SO}_2\text{CHCl}_2$. [59°]. Formed by treatment of $\text{C}_6\text{H}_5\text{SO}_2\text{CH}_2\text{CO}_2\text{H}$ with **Cl** in diffused daylight (Otto, *J. pr.* [2] 40, 511). Monoclinic prismatic tables, v. sol. hot alcohol.

PHENYL-CHLORO-NAPHTHYLAMINE. **Benzoyl derivative** $\text{C}_6\text{H}_5\text{NBz} \cdot \text{C}_6\text{H}_4\text{Cl}$. [152°]. Formed from **NPhBz**, $\text{C}_6\text{H}_5\text{I}$ and **PCl**₅ (Claus & Richter, *B.* 17, 1590). Needles, sol. alcohol.

PHENYL-CHLORO-NITRO-PHENYL-HYDRAZINE $\text{C}_6\text{H}_4\text{N}_2\text{H}_4\text{C}_6\text{H}_4\text{Cl}(\text{NO}_2)$ [1:4:6]. [140°]. Formed from phenyl-hydrazine and $\text{C}_6\text{H}_4\text{Cl}(\text{NO}_2)_2$ in the cold (Willgerodt, *J. pr.* [2] 37, 355). Red prisms (from alcohol and ether).

PHENYL TRI-CHLORO-OXY-PROPYL KETONE $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}(\text{OH})\text{CH}_2\text{Cl}$. [60°] and [77°]. Got from acetophenone, chloral, and **HOAc** (Koenigs, *B.* 25, 795). V. sl. sol. water. Converted by **H}_2\text{SO}_4** into $\text{C}_6\text{H}_5\text{COCH} \cdot \text{CH} \cdot \text{CCl}_2$ [102°].

PHENYL CHLORO-PHENYL HYDRAZINE $\text{C}_6\text{H}_5\text{N}_2\text{H}_4\text{C}_6\text{H}_4\text{Cl}$ [1:4]. [90°]. Formed by reducing $\text{C}_6\text{H}_5\text{N}_2\text{C}_6\text{H}_4\text{Cl}$ with alcoholic ammonium sulphide (Heumann & Mentha, *B.* 19, 1688).

PHENYL CHLORO-PHENYL KETONE v. **CHLORO-BENZOPHENONE**.

PHENYL-CHLORO-PROPIONIC ACID v. **CHLORO-PHENYL-PROPIONIC ACID**.

PHENYL *o*-CHLORO-*p*-TOLYL KETONE $\text{C}_6\text{H}_4\text{CO} \cdot \text{C}_6\text{H}_3\text{CH}_3\text{Cl}$. **Benzoylbenzyl chloride**. [98°]. Formed by chlorination of phenyl *p*-tolyl ketone at 110° (Thörner, *A.* 189, 89). Silky needles (from dilute alcohol). May be sublimed. On further chlorination at 135° it yields phenyl dichlorotolyl ketone or benzoyl benzylidene chloride $\text{C}_6\text{H}_4\text{CO} \cdot \text{C}_6\text{H}_3\text{CHCl}_2$ [96°] and, at 155°, phenyl tri-chloro-tolyl ketone or benzoyl-benzotrichloride $\text{C}_6\text{H}_4\text{CO} \cdot \text{C}_6\text{H}_2\text{CCl}_3$ [111°], which is converted by **PCl**₅ into $\text{C}_6\text{H}_4\text{CCl}_2 \cdot \text{C}_6\text{H}_2\text{CCl}_3$ [80°] crystallising in thin plates.

PHENYL-CHRYSYL-THIO-URBA $\text{C}_6\text{H}_5\text{NH} \cdot \text{CS} \cdot \text{NH} \cdot \text{C}_6\text{H}_4$. [186°]. Formed from phenyl-thiocarbamide and chrysyamine and from chrysyl-thiocarbamide and aniline in benzene solution (Aegg, *B.* 24, 957). Crystals.

PHENYL-CINCHONIC ACID v. **PHENYL QUINOLINE CARBOXYLIC ACID**.

PHENYL-CINCHONIDINE $C_{17}H_{15}PhN_2O$. Formed in two modifications (an oil, sol. ether, and an amorphous powder, insol. ether) by heating cinchonidine with aniline (Claus a. Batoche, B. 18, 2194). Both give $B^*H_2PtCl_2$ 2aq.

PHENYL-CINNAMIC ACID $C_{15}H_{11}O_2$ i.e. $C_6H_5CH:CH.COPh.CO_2H$. [170°]. Formed by saponifying the nitrile or heating sodium phenylacetate with benzoic aldehyde and Ac_2O at 150° (Oglialoro, G. 9, 429). Needles, sol. alcohol and ether, v. sl. sol. cold water. Reduced by sodium-amalgam to $\alpha\beta$ -di-phenyl-propionic acid. — BaA' , 4aq: micaceous plates.

Methyl ether MeA' . [78°] (Cabella, G. 14, 114). Needles (from dilute alcohol).

Nitrile $C_6H_5CH:CH.CPh.CN$. *Phenyl-styryl cyanide*. [87°]. (360° cor.). Formed by the action of benzy cyanide on benzoic aldehyde or benzyldene chloride in presence of $NaOAc$ or solid $NaOH$ (Rossolyma, B. 22, 1235; Meyer, A. 250, 124; Janssen, A. 250, 129; Neure, A. 250, 155; Frost, A. 250, 157). White plates (from alcohol). Yields $CHPhBr.CPhBr.CN$ [130°] and $CHPhCl.CPhCl.CN$. [168°].

α -Carboxylic acid. Imide
 $C_6H_5 \begin{array}{l} \diagup C(CHPh).CO \\ \diagdown CO \end{array} NH$ [174°]. Formed by heating the imide of carboxy-phenyl-acetic acid (vol. i. p. 706) with benzoic aldehyde (Gabriel, B. 20, 1205). Needles.

References.—Nitro- and Oxy- PHENYL-CINNAMIC ACID.

PHENYL-CINNAMYL-HYDRAZINE
 $CHPh:CH.CH_2.NPh.NH_2$ [54°]. Formed from sodium phenyl-hydrazine and cinnamyl bromide (Michaelis, B. 22, 2233). Crystals.

PHENYL-CINNAMYL KETONE v. PHENYL STYRYL KETONE.

PHENYL-p-COUMARIC ACID [1:4]
 $C_6H_4(OH).CH:CH.CO_2H$ [219°]. Formed by heating p-oxy-benzoic aldehyde with Ac_2O and sodium phenyl-acetate and boiling the resulting acetyl derivative with baryta-water (Oglialoro, G. 13, 173). — AgA' : nearly insol. water.

Acetyl derivative. [170°].

Methyl ether MeA' . [170°].

Ethyl ether EtA' . [152°].

Methyl derivative. [489°]. Vol. iii. p. 738.

PHENYL-COUMARIN $C_{15}H_{10}O_2$ [140°]. Formed, together with $C_6H_5(OAc).CH:CH.CO_2H$, by heating salicylic aldehyde with sodium phenyl-acetate and Ac_2O for 8 hours at 150° (Oglialoro, G. 9, 428). Prisms, sol. ether.

Mono-sulphonic acid $C_6H_4(O_2S)H$ 2½aq. [263]. White needles (Curatolo, G. 14, 457).

— BaA' , — PbA' , 4aq: needles, m. sol. hot water.

Di-sulphonic acid $C_6H_4(O_2S)_2$, 6aq. [89°]. Deliquescent crystals. — BaA' , 4aq: white prisms. — PbA' , 5aq: needles, v. sol. watgr.

PHENYL-CROTONIC ACID $C_{10}H_8O_2$ i.e. $C_6H_5.CH:CH.CO_2H$. *Phenyl-methacrylic acid*. (α)-*Methyl-cinnamic acid*. [82°]. Formed by heating benzoic aldehyde with propionic anhydride and sodium propionate (Perkin, C. J. 31, 391; 32, 661). Formed also by heating benzoic aldehyde with Ac_2O and sodium methyl-malonate; and by heating benzoic aldehyde with sodium propionate and $HOAc$ or Ac_2O (Stuart, C. J. 43, 404; Slocum, A. 227, 57). Obtained also by oxidation of the corresponding aldehyde (Miller a. Klein, B. 19, 526). It is also a product of the

action of Na on benzyl propionate (Conrad a. Hodgkinson, A. 193, 814).

Transparent plates (from alcohol), sl. sol. hot water. When prepared by Perkin's method it appears to be accompanied by an isomeride [74°] crystallising in needles, which is converted into the acid [82°] by frequent recrystallisation (Raikoff, B. 20, 3396). Yields methanol (q. v.) when heated with dilute H_2SO_4 . Bromine forms $CHPhBr.CMeBr.CO_2H$ [137°] (Körner, B. 21, 276).

Salts.— BaA' , aq: very minute plates. — BaA' , 4aq: small white crystals, got by slow cooling. — AgA' . S. 374. Needles.

Methyl ether MeA' . [39°]. (254°).

Amide [128°] (Edeleago, B. 20, 619).

Phenyl-isocrotonic acid

$C_6H_5.CH:CH.OH.CO_2H$ [86°] (J.); [88°] (B. a. D.). (302°). Formed by heating benzoic aldehyde with succinic anhydride and sodium succinate (Perkin), the yield being 2 p.c. (Jayne, A. 213, 100). Formed also by heating phenyl-trimethylene tricarboxylic acid $C_6H_5Ph(CO_2H)_3$ in a current of CO_2 at 190° (Buchner a. Dessauer, B. 25, 1155). Prepared by heating benzoic aldehyde with sodium succinate and Ac_2O at 125°, and separated from phenyl-paraconic acid by solution in CS_2 . Long thin needles (from water) or prisms (from CS_2). When heated with H_2SO_4 (4 pts.) and water (4 pts.) it changes to the isomeric phenyl-butyrolactone and an acid [179°] (Erdmann, A. 227, 257). Yields γ -phenyl-butyric acid [49°] on reduction. Boiling $NaOH$ aq converts it into the isomeric $C_6H_5.CH_2.CH:CH.CO_2H$ [65°]. Split up by long boiling into water and (α)-naphthol. Alkaline $KMnO_4$ at 0° forms di-oxy-phenyl-butyric lactone (Fittig a. Obermüller, A. 268, 44). — BaA' , 8aq. — CaA' , 8aq. — AgA' : bulky pp.

α -Phenyl-crotonic acid $CH_3.CH:CH.CO_2H$. *Methylatropic acid*. [185°]. Formed by heating sodium phenyl-acetate with paraldehyde and Ac_2O (Oglialoro, G. 15, 514). Minute prisms (from water), sol. alcohol and ether. — AgA' : m. sol. hot water.

Phenyl-crotonic acid

$C_6H_5.CH:C(CHPh).CO_2H$. [158°]. Formed from sodium phenyl-propionate, benzoic aldehyde, and Ac_2O at 160° (Oglialoro, G. 20, 162). Needles (from alcohol).

Reference.—Oxy-PHENYL-CROTONIC ACID.

PHENYL-CROTONIC ALDEHYDE v. PHENYL-METHACRYLIC ALDEHYDE.

PHENYL-CUMAZONIC ACID

$C_{17}H_{15}NO$ i.e. $C_6H_5(CO_2H) \begin{array}{l} \diagup CMe_2O \\ \diagdown N=CPh \end{array}$ (?). [220°]. Formed by heating (3,4,1)-amido-oxypropyl-benzoic acid with $BzCl$ at 100°–120° (Widmann, B. 16, 2585). White crystals. Sol. alcohol, insol. water. — $HA'H_2SO_4$, 2aq: thin plates.

PHENYL-CUMINYL-AMINE $C_{15}H_{13}N$ i.e. $C_6H_5.NH.CH_2.C_6H_4.Pr$. [41°]. Formed by reducing $C_6H_5.N:CH.C_6H_4.Pr$ (Uebel, A. 245, 289). Plates or prisms. Yields a nitrosamine $C_{15}H_{13}(NO)N$ [94°]. — B^*HCl : white crystals.

PHENYL-CUMINYL-THIO-UREA

$C_6H_4.Pr.CH_2.NH.CS.NHPh$. [100°–106°]. Formed from cuminyllamine and phenyl-thiocarbimide (Goldschmidt a. Gessner, B. 20, 2416).

PHENYL-CUMINYL-UREA $C_{15}H_{13}N_2O$ i.e. $C_6H_5.NH.CO.NH.C_6H_4.Pr$. [144°]. Formed from cuminyl cyanate and aniline (Baab, B. 8, 1151).

Essner & Gossin, *Bl.* [2] 42, 179). Liquid. Fields an acetyl derivative boiling above 160° and a benzoyl derivative [75°].

DI-PHENYL DURENE DIKETONE $C_{18}H_{10}O_2$, i.e. $(C_6H_5CO)_2CMe_2$. [270°]. (above 180°). Formed from durenene, $BzCl$, and $AlCl_3$, Friedel & Crafts, *A. Ch.* [6] 1, 512. Prisms.

PHENYL DURENE KETONE $C_{17}H_{10}O$ i.e. $C_6H_5COCHMe_2$. [119°]. (343°) at 725 mm. Not from durenene, $BzCl$, and $AlCl_3$ (Friedel & Crafts, *A. Ch.* [6] 1, 511). Acicular prisms, v. sol. in warm alcohol. Reduced by HI and P to C_6H_5 , 80-85° (310° at 716 mm.). Br_2 forms $C_{17}H_9Br_2O$ [225°] and other products.

Phenyl isodurene ketone. [63°]. (300°). Formed by the action of $BzCl$ and $AlCl_3$ on the isodurenene derived from toluene (Essner & Gossin, *Bl.* [2] 42, 170). Sublimative treatment with HCl and alcoholic potash gives the acid $C_6H_5Me_2CPh(OH)CO_2H$, sol. water and alcohol.

PHENYLENE. The radical C_6H_5 .

PHENYLENE-ACETAMIDINE

$C_6H_5\langle\begin{smallmatrix} NH \\ N \end{smallmatrix}\rangle C_6H_5$. [170°] (H); [175°] (L).

Formed by boiling phenylene-*o*-diamine with $HOAc$, or by reducing $C_6H_5(NO_2)(NHAc)$ with tin and HCl (Ladenburg, *B.* 8, 677; Hübner, *A.* 209, 353). Needles. $BHCl$. $B'H_2PtCl_6$ aq. $B'HNO_2$. $B'H_2SO_4$.

Phenylene-di-acetamidide $C_{10}H_{11}N$, i.e. [1:4] $C_6H_4(CH_2C(NH)NH_2)_2$. [182°]. Formed by the action of alcoholic NH_3 , followed by $NaOH$ aq. upon the hydrochloride of phenylene-di-acetimidide-ether (Glock, *B.* 21, 2660). Plates.

***o*-PHENYLENE-DI-ACETIC ACID** $C_{10}H_8O_4$, i.e. [1:2] $C_6H_4(CH_2CO_2H)_2$. Mol. w. 194. [150°]. Formed by saponification of its nitrile by boiling with dilute H_2SO_4 (Baeyer & Pape, *B.* 17, 449). Slender needles, v. sol. alcohol, m. sol. cold water. AgA'' ? insoluble pp.

Nitrile $C_6H_4(CH_2CN)_2$. [60°]. Formed by the action of KCy on di-*o*-bromo-*o*-xylene.

***m*-Phenylene-di-acetic acid** $C_{10}H_{10}O_4$, i.e. [1:3] $C_6H_4(CH_2CO_2H)_2$. [170°]. Formed by boiling its nitrile with alcoholic potash (Kipping, *C. J.* 53, 42; *B.* 21, 42). Needles, v. sol. water. AgA'' : white pp.

Nitrile $C_6H_4(CH_2CN)_2$. [29°]. (308° at 300 mm.). From [1:3] $C_6H_4(CH_2Br)_2$ and KCy .

***p*-Phenylene-di-acetic acid** $C_6H_4(CH_2CO_2H)_2$. [241°]. Got from its nitrile (Biedermann, *B.* 5, 703; Klippert, *B.* 9, 1766; Kipping, *C. J.* 53, 44). Needles, m. sol. water. $CaA''2aq$. $CaA''2aq$. ZnA'' . CaA'' . AgA'' : white amorphous pp.

Ethers. MeA'' . [57°]. EtA'' . [58°].

Chloride. Oil (Klippert).

Amide. (above 290°). Plates and needles.

Nitrile $C_6H_4(CH_2CN)_2$. [98°]. Formed by the action of KCy on $C_6H_4(CH_2Br)_2$ or $C_6H_4(CH_2Cl)_2$. Three-sided prisms (from ether). Alcoholic ammonium sulphate at 100° converts it into $C_6H_4(CH_2CS.NH_2)_2$ [206°] which crystallises from H_2O .

Di-phenylene-acetic acid $C_6H_5\langle\begin{smallmatrix} CH_2 \\ C \end{smallmatrix}\rangle CH_2CO_2H$. [222°]. Formed by heating $C_6H_5C(OH)CO_2H$ with HI and P at 140° (Friedländer, *B.* 10, 538). Small crystals (from alcohol). Decomposed by heating with soda-lime into CO_2 and fluorene. AgA'' : unstable pp.

Ethyl ether EtA'' . [165°].

Reference.—OXY-DIPHENYLENE-ACETIC ACID.

***p*-PHENYLENE-DI-ACETIMIDO-ETHER**

$C_6H_4(CH_2C(NH)OEt)_2$. The hydrochloride $B'H_2HCl$ [above 240°] formed by the action of alcohol and HCl on $C_6H_4(CH_2CN)_2$, crystallises in needles (Glock, *B.* 21, 2660). It is insol. ether.

***o*-PHENYLENE-DI-ACRYLIC ACID**

$C_6H_4(CH_2CH.CO_2H)_2$. [above 300°]. Formed by boiling $C_6H_4(CH_2CO_2Et)_2$ with alcoholic potash (Perkin, *C. J.* 53, 14; *B.* 19, 436). Sl. sol. water, v. sl. sol. alcohol. AgA'' : pp.

***p*-Phenylene-di-acrylic acid**

$C_6H_4(CH_2CH.CO_2H)_2$. [310°]. Obtained by saponifying the mono-ethyl ether $HEtA''$ [300°] which is got by heating *p*-aldehyde-cinnamic ether with $NaOAc$ and Ac_2O (Löw, *A.* 231, 377). Got also by boiling $C_6H_4(CH_2.CBr(CO_2Et))_2$ with alcoholic potash (Kipping, *C. J.* 53, 41). Yields a tetrabromide crystallising in needles. AgA'' .

PHENYLENE-DI-ALLYL-DI-THIO-DI-UREA $C_6H_4(NH.CS.NHCO_2H)_2$. The *o*- [159°], *m*- [105°], and *p*- [200°] compounds are formed by heating the corresponding phenylene-diamines with alcohol and allyl-thiocarbamide (oil of mustard) at 100° (Lellmann & Würthner, *A.* 223, 201). The *o*- and *p*- compounds decompose when heated. They are all sol. $HOAc$.

***o*-PHENYLENE-DI-AMIDO-DI-ACETIC ACID** [1:2] $C_6H_4(NHCH_2CO_2H)_2$. The ether EtA'' [135°] is got from *o*-phenylene diamine and $ClCO_2Et$ (Zimmermann & Knyrim, *B.* 16, 515).

***m*-Phenylene-di-amido-di-acetic acid**

[1:3] $C_6H_4(NHCH_2CO_2H)_2$. The ethyl ether EtA'' [78°] is got by heating *m*-phenylene-diamine with $OH.Cl.CO_2Et$ (Zimmermann, *B.* 15, 518; 16, 514). It is converted by conc. HCl aq. into crystalline $H_2A''H_2Cl$, v. sol. water.

***p*-Phenylene-di-amido-di-acetic acid**. The ethyl ether EtA'' [83°] and the hydrochloride, $H_2A''H_2Cl$, are formed in like manner from *p*-phenylene-diamine.

***o*-PHENYLENE-DIAMINE** [1:2] $C_6H_4(NH_2)_2$. Mol. w. 108. [104°]. (252°). Prepared by reducing *o*-nitro-aniline with tin and HCl (Zincke & Sintenis, *B.* 6, 123; Vignon, *Bl.* [3] 2, 675; Sandmeyer, *B.* 19, 2654). Formed also by heating the corresponding di-amido-benzoic acids with baryta (Griess, *J. pr.* [2] 8, 143; Salkowski, *A.* 173, 58) and by the action of tin and HCl on bromo-*o*-nitro-aniline (Wurstler, *A.* 171, 63; Hübner, *A.* 209, 360) and on *o*-di-nitro benzene (Zincke, *B.* 7, 1874). Plates (from water) or tables (from chloroform), v. e. sol. hot water, alcohol, and ether.

Reactions.—1. $FeCl_3$ added to a solution of the hydrochloride forms di-amido-phenazine hydrochloride, which crystallises in ruby-red needles $C_{12}H_{10}N_4HCl$ (Fischer, *B.* 22, 355).—2. *Pyrocatechin* at 200° forms phenazine $C_{12}H_8N_4$; C_6H_5 . (3) *Naphthoquinone* forms naphthophenazine $C_{18}H_{10}N_4$; C_6H_5 .—4. *Cyanogen* gas forms $C_6H_5N_4$, a yellow crystalline powder (c. 280°), sl. sol. water, forming $B'H_2PtCl_6$ aq and $B'H_2PtCl_6$ aq. By heating with HCl it is converted into $C_6H_5N_4O$ [280°] and di-oxy-quinazoline (Bladin, *Bl.* [2] 42, 104; *B.* 18, 872).—5. The *sulphocyanide* is converted by heat into a mixture of phenylene-thio-urea and thio-urea (Lellmann, *A.* 221, 8).—6. KNO_3 added to a very dilute solution of the sulphate forms 'amidazo-phenylene' $C_6H_5N_4$.

PHENYLENE-DIAMINE

...from benzene in pearly white needles [88-5°] (Ladenburg, *B.* 9, 219).—7. ICy forms C_6H_5N , which yields the salts $B^+H_2Cl_2$, B^+HCl_2 , B^+HNO_3 , $B^+H_2SO_4$, and the benzoyl derivative C_6H_5BaN , and is converted by nitrous acid into $C_6H_5N_2O$ (Hübner, *B.* 9, 778; 10, 1716).—8. The hydrochloride is converted by benzoic aldehyde into dibenzylidene-phenylene diamine $C_{12}H_{10}(N:CHPh)_2$ [184°], yielding $B^+H_2P_2Cl_4$, B^+HNO_3 , $B^+H_2SO_4$, B^+MeI , and B^+EtI [218°] (Ladenburg, *B.* 11, 1658).

Salts.— B^+HCl . Needles, v. sol. water.— $B^+H_2P_2Cl_4$.— $B^+H_2SO_4$.— $B^+H_2SO_4$, 1:1 aq: plates.

Di-acetyl derivative $C_6H_5(NHAc)_2$, [186°]. Long silky needles, v. sol. hot water and alcohol (Bistrzycki, *B.* 23, 1878).

Benzoyl derivative $C_6H_5(NH_2)(NHbz)$, [140°]. Got by reducing $C_6H_5(NO_2)(NHbz)$ with ammonium sulphide (Mixer, *Am.* 6, 26). Minute crystals, sol. water. When the reduction is effected by tin and HCl the product is benzenyl-phenylene-diamine (*q. v.*).

Dibenzoyl derivative $C_6H_5(NHbz)_2$, [*q.* 300°]. Thin prisms (from HOAc) (Bistrzycki).

Di-*p*-toluyl derivative $C_6H_5(NH.CO.C_6H_4Me)_2$, [228°]. Got, together with tolenyl-benzamidine $C_6H_5.NH.C_6H_4Me$ [268°], by the action of *p*-toluyl chloride on *o*-phenylene-diamine dissolved in benzene (Hübner, *A.* 210, 828). Colourless needles, sl. sol. alcohol.

m-Phenylene-diamine $C_6H_5(NH_2)_2$, [63°] (277° i.v.). Prepared by reduction of *m*-di-nitro-benzene or *m*-nitro-aniline (Hofmann, *Pr.* 11, 618; 12, 639; Zincke, *B.* 5, 792). Formed also by heating *s*-di-amido-benzoic acid with baryta (Wurster, *B.* 7, 214; Hübner, *A.* 222, 86), and by the action of tin and HCl on (4,2,1)-di-nitro-benzoic acid (Wurster, *B.* 7, 149) and on (1,3,4)-bromo-di-nitro-benzene (Z.). Got also by heating resorcin (1 pt.) with ammoniacal $CaCl_2$ (4 pts. containing 35 p.c. NH_3) for eight hours at 275° (Seyewitz, *C. R.* 109, 814). Crystalline, m. sol. water, v. sol. alcohol and ether. Its solutions are alkaline in reaction. KNO_3 added to a solution of a salt of *m*-phenylene-diamine forms a brown pp. containing $C_6H_5(NH_2)_2.N_2.C_6H_5.NH_2$. A solution in dilute H_2SO_4 is coloured yellow by a trace of nitrous acid. Aldehyde added to an alcoholic solution of *m*-phenylene-diamine hydrochloride forms an orange-red colour, with a green fluorescence. From this liquid NH_4 aq. ppt. di-methyl-phenanthroline tetrahydride $C_{12}H_{10}N_4$ (Girard a. Roques, *C. R.* 107, 1158; Schiff, *A.* 253, 828). Benzoic aldehyde in alcohol forms with the hydrochloride the base $CHPh(C_6H_5(NH_2)_2)$. The hydrochloride of *m*-phenylene-diamine gives a crimson colour when boiled with oxygenated water (Denigès); in presence of ammonia the liquid becomes blue, but is turned red by $NaOH$ aq. Hydrogen peroxide gives a bluish-green tint (Cazeneuve, *Bl.* [3] 5, 855). PbO_2 and dilute $HOAc$ give a brown colour (Lauth, *C. R.* 111, 975). Alkaline $NaOBr$ gives a maroon-red pp. (Denigès, *C. R.* 107, 662). CS_2 in alcohol at 35° forms yellow monoclinic prisms of $C_6H_5\langle\begin{smallmatrix} NH \\ NH \end{smallmatrix}\rangle CS$ and several other bodies (Guoci, *G.* 17, 523, 2657). The sulphocyanide is converted by heat into $C_6H_5(NH.CS.NH_2)$, (Lellmann, *A.* 221, 8). *m*-Phenylene-diamine is somewhat less poison-

ous than the *p*-isomeride [Dubois a. Vignon, *C. R.* 107, 533].

Salts.— B^+HCl . Needles, v. sol. water, sl. sol. conc. HCl aq.— B^+HCl .— $B^+H_2P_2Cl_4$: needles.— $B^+H_2SO_4$ (Gerdemann, *Z.* [9] 1, 51).— $B^+H_2SnCl_4$.— $B^+H_2SO_4$.

Hydriodide: Mills, *C. J.* 17, 153.

Di-formyl derivative $C_6H_5(NH.CHO)_2$, [155°]. Small crystals (Tobias, *B.* 15, 2447).

Mono-acetyl derivative

$C_6H_5(NH_2)(NHAc)$. Crystalline solid, v. sol. water (Wallach a. Schulze, *B.* 15, 3020).— B^+HCl , [280°].

Di-acetyl derivative $C_6H_5(NHAc)_2$, [189°] (Kelbe, *B.* 16, 1200; cf. Barbaglia, *B.* 7, 1257).

Mono-benzoyl derivative

$C_6H_5(NH_2)(NHbz)$, [125°] (Bell, *B.* 7, 498); [260°] (Hübner, *AP.* 208, 298). Got by reducing $C_6H_5(NO_2).NHbz$.— B^+HCl .— $B^+H_2SO_4$. Needles.

Di-benzoyl derivative $C_6H_5(NHbz)_2$, [240°] (Ruhemann, *B.* 14, 2651; Hinsberg, *A.* 254, 255). White plates.

m-Amido-benzoyl derivative

$C_6H_5(NH_2)(NH.CO.C_6H_4NH_2)$, [129°]. Needles (from dilute alcohol) (Hugh, *B.* 7, 1268).

o-Oxy-benzoyl derivative

$C_6H_5(NH_2).NH.CO.C_6H_4.OH$, [143°]. Crystals (Bell, *C. J.* 28, 1201).

p-Phenylene-diamine $C_6H_5(NH_2)_2$, [140°] (267°).

Formation.—1. By reduction of *p*-nitro-aniline and of *p*-di-nitro-benzene (Hofmann, *Pr.* 11, 518; 12, 639; Zincke, *B.* 7, 871).—2. By reduction of $C_6H_5.N.C_6H_4.NH_2$ (Martius a. Griess, *Z.* 1866, 136).—3. By distilling (5,2,1)-di-amido-benzoic acid (Griess, *B.* 5, 201).—4. In the preparation of induline by heating $C_6H_5.N_2.C_6H_4.NH_2$ with aniline hydrochloride (Witt; Fischer a. Hepp, *B.* 23, 839).

Preparation.—From acetanilide by nitration and reduction with tin and HCl.

Properties.—Plates (by sublimation) or monoclinic crystals (from water) changing in the solution to trimetric plates. M. sol. water, v. sol. alcohol and ether. Forms a hydrate $C_6H_5N_2.2aq$ [80°]. With PbO_2 and aqueous $HOAc$ it gives a bright bluish-green colour (Lauth, *C. R.* 111, 975). *p*-Phenylene-diamine is very poisonous (Vignon, *C. R.* 107, 533). A mere trace of a mixture of *m*- and *p*-phenylene-diamine gives on warming with $HOAc$ and $K_2Cr_2O_7$ a blue colour, changing on boiling to red (Witt, *C. J.* 35, 356; Meldola, *C. J.* 51, 105).

Reactions.—1. Oxidised to quinone by H_2SO_4 and MnO_2 . Quinone is also formed together with NH_3 by oxidation of the sulphate with $K_2Cr_2O_7$ (Meldola a. Evans, *C. J.* *F.* 6, 115).—2. When exposed to air, O_2 , H_2O_2 or K_2FeO_4 , *p*-phenylene-diamine and its salts are oxidised to $C_6H_5N_2$, a feeble red base with green lustre [230°] yielding $C_6H_5AcN_2$ [294°] (Bandrowski, *M.* 10, 126).—3. Chlorine passed into a solution in $HOAc$ forms tetra-chloro-quinone.—4. $FeCl_3$ added to a solution of the hydrochloride saturated with H_2S ppt. Lauth's violet, which is v. sol. pure water, but pp. by salts (Lauth, *C. R.* 82, 1441).—5. Potassium nitrite added to a solution of the hydrochloride forms $C_6H_5(NH_2)N_2Cl$, and in presence of a large excess of HCl it forms $C_6H_5(N_2Cl)_2$.—6. Mixed

with aniline (2 mols.) and oxidised by $K_2Cr_2O_7$, it yields pheno-safranin.—7. The *sulphocyanide* is converted by heat into $C_6H_5(NH.CS.NH)_2$ (Lellmann, A. 221, 8).—8. *Bleaching-powder* solution added to a solution in $HClAq$ ppts. yellowish-white quinone-di-chloro-di-imide which detonates at 124° (Krause, B. 12, 47).—9. *Aceto-acetic ether* at 170° forms $C_6H_5(NH.CO.CH_3)_2$ which is probably $C_6H_5(NH.CO.CH_3)_2$ (Knorr, B. 17, 545; 197 3303).

Salts.— $B''H.Cl$. Triclinic tables, v. sol. water, almost insol. $HClAq$.— $B''H.PtCl_4$.— $B''H.SnCl_4$ (Hübner, A. 208, 366).— $B''H.Br$.— $B''H_2SO_4$ (Bernthsen, A. 251, 62).— $B''H_2SO_4$. Micaceous plates, sl. sol. water (Vignon, Bl. [2] 50, 152).— $B''H_2CO_3$. S. 15 at 15° .

Di-formyl derivative $C_6H_5(NH.CHO)_2$. [204°]. Amorphous mass (Wundt, B. 11, 828).

Mono-acetyl derivative $C_6H_5(NH.CO.CH_3)$. [161°]. Formed by reduction of $C_6H_5(NO_2).NHAc$ with iron and acetic acid (Nietzki, B. 17, 343). Needles, sl. sol. cold water.— $B''H.PtCl_4$.

Di-acetyl derivative $C_6H_5(NH.CO.CH_3)_2$. [above 235°]. Formed by boiling the base with $HOAc$ (Biedermann, A. Ledoux, B. 7, 4531). Small octahedra, sol. $HOAc$.

Benzoyl derivative $C_6H_5(NH)(NHBz)$. [128°]. Formed by reducing benzoyl-*p*-nitro-aniline (Hübner, A. 208, 295). Plates, sl. sol. water.— $B''HCl$.— $B''H_2SO_4$. Needles.

Di-benzoyl derivative $C_6H_5(NH)(NHBz)_2$. [above 300°]. Formed from the base, $BzCl$, and $NaOHAc$ (Hinsberg, A. 254, 254). Plates. Yields a nitro-product [251°].

o-Oxy-benzoyl derivative $C_6H_5(NH)(NH.CO.C_6H_4.OH)$. [158°]. Glittering needles (Bell).

Hexahydride $C_6H_6(NH)_2$. *Di-amido-hexamethylene*. Formed by reducing the di-oxim of quinone tetrahydride in alcohol with Na (Baeyer, A. Noyes, B. 22, 2172). Liquid, with faint ammoniacal odour, forming crystalline salts and an acetyl derivative melting above 310° .

References.—Bromo, Bromo-nitro, Chloro-, Nitro-, and Oxy-phenylene-diamine.

PHENYLENE-DIAMINE SULPHONIC ACID v. DI-AMIDO-BENZENE SULPHONIC ACID.

PHENYLENE-DI-AMYL-DIAMINE [1:4] $C_6H_5(NH.C_4H_9)_2$. [48°]. Colourless crystals (Baeyer, A. Noyes, B. 22, 2173).

DIPHENYLENE-AZONE $C_6H_5.N=N.C_6H_5$. [156°].

Formed, together with $C_{12}H_8N_2O_2$ [240°] and $C_{12}H_8N_2O$ [152°] by boiling di-*o*-nitro-diphenyl with alcohol and zinc-dust (Täuber, B. 24, 3081, 3883). Greenish-yellow needles by sublimation, not volatile with steam. Almost insol. water, v. sol. alcohol, m. sol. ether, v. e. sol. $HOAc$. Reduced by tin and HCl to $C_{12}H_{10}N_2.HCl$, which crystallises in white needles, rapidly re-oxidised by air to diphenylene-azone.

Salts.— $B''HCl$. Flat bronzed prisms.— $B''H.AuCl_4$.— $B''H.PtCl_4$: yellow needles.— $B''H.CrO_4$.— $B''C_6H_5N_2O_2$. [194°]. Brown needles.

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PHENYLENE-BENZAMIDINE v. BENZYL-PHENYLENE-DIAMINE.

VOL. IV.

PHENYLENE-DI-BENZIDENE-DIAMINE v. DI-BENZYLIDENE-PHENYLENE-DIAMINE.

PHENYLENE-BENZYL-*m*-DIAMINE $C_6H_5(NH_2).NHC_6H_4$. Formed by reducing benzyl-*m*-nitro-aniline (Meldola, A. Coste, C. J. 55, 537). Oil.— $B''2HCl$: hexagonal tablets. $FeCl_3$ colours its solution red and gives a white pp. on heating.

Di-benzoyl derivative $C_6H_5(NHBz).NBz.C_6H_5$. [178°]. Sol. in alcohol.

Phenylene-benzyl-*p*-diamine. [30°]. Got by reducing benzyl-*p*-nitro-aniline (Meldola, A. Coste, C. J. 55, 590) or *p*-nitroso-benzyl-aniline (Boeddinghaus, A. 263, 302). Wax-like mass of crystals, turning red in air. When mixed with the *m*-isomeride it yields di-benzyl-amido-indamine on oxidation.— $B''2HCl$. White plates, v. sol. water. $FeCl_3$ colours its aqueous solution green, changing to red. After saturation with H_2S it gives a blue pp. with $FeCl_3$.

Di-acetyl derivative. [117°]. Prisms.

Di-benzoyl derivative. [124°]. Needles.

Phenylene-di-benzyl-diamine v. vol. i. p. 501.

Phenylene-tetra-benzyl-*m*-diamine $C_6H_5(N(C_6H_5)_2)_2$. [81°]. Formed by heating phenylene-*m*-diamine with $NaOHAc$ and benzyl chloride. Amorphous powder, sol. $HOAc$.

Phenylene-tetra-benzyl-*p*-diamine. [149°]. White crystalline powder. $HOAc$ and CrO_3 form a blue-violet colouring matter.

PHENYLENE - BENZYLIDENE - DI - METHYL-DIAMINE $C_6H_5.N_2$ i.e.

$C_6H_5.CH.N(C_6H_5).NMe_2$. [93°] (Calm, B. 17, 2940); [101°] (Köhler, A. 241, 361). Formed from phenylene-di-methyl-*p*-diamine and benzoic aldehyde.— $B''2HCl$.

PHENYLENE - BENZYL - DI - METHYL - DIAMINE $C_6H_5.CH_2.NH.C_6H_5.NMe_2$. [48°]. Formed by reducing the preceding body in alcohol with sodium-amalgam (Köhler, A. 241, 361). Plates. Yields a nitrosamine [128°].

PHENYLENE-BLUE or *Taurth's violet* v. AMIDO-IMIDO-DI-PHENYL-SULPHIDE.

PHENYLENE - BROMO - ACETYLENE - KETONE v. BROMO-OXY-INDONAPHTHENE.

DI-PHENYLENE-BUTANE $C_6H_5.CH_2.CH_2.C_6H_5$ or $CH_3.CH(C_6H_5)_2$.

Diphensuccindene. [100°]. Formed by heating (β)-di-phenyl-succinic anhydride with HI and P and 180° (Roser, A. 247, 156). White needles.

PHENYLENE-ISOBUTYL-*p*-DIAMINE

$C_6H_5.NH.C_4H_9.NH_2$. [39°]. Formed by reduction of *p*-nitroso-isobutyl-aniline (Wacker, A. 243, 299). Plates (from benzene-ligroin).

PHENYLENE - BUTYLIDENE-*o*-DIAMINE

$C_6H_5.NH.C_4H_9.NH_2$. [233°]. Formed from phenylene-*o*-diamine and isobutyric aldehyde (Lassar-Cohn, B. 22, 2724). Needles (by sublimation).— $B''HCl$. [184°].— $B''H_2PtCl_4$.

The isomeric compound from phenylene-*m*-diamine melts at 216° , while that from phenylene-*p*-diamine is oily, and yields $B''H.PtCl_4$.

DI - PHENYLENE - ISOBUTYL - QUINOX-

ALINE $C_6H_5.C:N.C_6H_5$ or $C_6H_5.CH_2.Pr$. [247°]. Formed from phenanthraquinone in $HOAc$ and isobutyl-phenylene-diamine in alcohol (Gelzer, B. 20, 8256). Yellowish needles.— $B''HCl$: needles.

***o*-PHENYLENE-DICARBAMIC ETHER**

$C_6H_5(NH.CO.Et)_2$. [88°]. Formed by heating

C

(Otto, *J. pr.* [3] 36, 450). White plates, m. sol. conc. HNO_3 .

PHENYLENE DI-ETHYL DIKETONE

$\text{C}_6\text{H}_4(\text{CO}_2\text{C}_2\text{H}_5)_2$ [220°]. Formed from terephthalic chloride and ZnEt_2 in ether (Münchmeyer, *B.* 13, 1850). Needles (from ether).

PHENYLENE DI-ETHYL DISULPHONE

$\text{C}_6\text{H}_4(\text{SO}_2\text{Et})_2$ [142°]. Obtained by heating $\text{C}_6\text{H}_4(\text{SO}_3\text{K})_2$ [1.0] with EtBr at 100° (Otto, *J. pr.* [2] 36, 449). Colourless plates.

PHENYLENE-FURFURALDEHYDINE v.

vol. i. p. 109.

PHENYLENE-DIGLYCOLLIC ACID v. Oxydiphenylene-acetic acid.

DIPHENYLENE-DIHYDRAZINE $\text{C}_{12}\text{H}_{10}\text{N}_4$, i.e. $\text{N}_2\text{H}_2\cdot\text{C}_6\text{H}_4\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\text{H}_2$ [167°]. Formed from benzidine hydrochloride by diazotisation and reduction by Na_2SO_3 or SnCl_2 (Arheideit, *A.* 239, 206). Small white plates, sol. hot water. Aqueous potassium cyanate forms the semicarbazide $\text{C}_{12}\text{H}_{10}\text{N}_6\text{O}_2$ [307°]. Nitrous acid forms a di-nitrosamine $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_2$ [112°]. Pyruvic acid forms $\text{C}_{12}\text{H}_{10}\text{N}_4\text{O}_4$ [197°]. Acetone yields $\text{C}_{12}\text{H}_{10}\text{N}_4$ [198°], whence fusion with ZnCl_2 yields diphenyl-di-methyl-indole $\text{C}_{12}\text{H}_{10}\text{N}_2$ [270°].

• *Reference.*—Di-oxy-di-phenylene dihydrazine.

DIPHENYLENE-IMIDE v. Carbazole.

DIPHENYLENE KETONE

[83°]. (Above 300°).

Formation.—1. By distilling phenanthraquinone or diphenyl di-o-carboxylic acid with CaO (Fittig a. Ostermayer, *A.* 166, 373; Anschütz a. Schultz, *B.* 9, 1400).—2. By heating anthraquinone with lime (Anschütz, *B.* 11, 1213).—3. By dry distillation of the Ag salt of its dicarboxylic acid (Bamberger a. Hooker, *B.* 18, 1034; *A.* 229, 156).—4. By passing a mixture of phenol and CS_2 over hot copper (Carnelley a. Dunn, *C. J. Proc.* 4, 53; *B.* 21, 2005, who regard the product thus obtained as isomeride).

Properties.—Yellow needles or plates (from alcohol). Yields phenyl-benzoic acid by potash-fusion. Distillation over zinc-dust gives diphenylene-methane [113°] (Fittig, *B.* 6, 187). Forms a nitro-derivative [220°] and a di-nitro-derivative [290°] (Schultz, *A.* 203, 104). Alkaline KMnO_4 oxidises it to phthalic acid (Anschütz a. Japp, *B.* 11, 213). H_2SO_4 forms at 260° a disulphonic acid, whence CaA'' (Schmidt a. Schultz, *A.* 207, 345).

Oxim. [192°] (Spiegler, *M.* 5, 195).

References.—Bromo-, Di-chloro-, Nitro-, and Oxy-, DIPHENYLENE KETONE.

DIPHENYLENE KETONE CARBOXYLIC

ACID [1.2] $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ [1.6]. [192°].

Formed by oxidation of fluoranthene by chromic acid mixture (Fittig, *A.* 193, 149; 200, 6). Orange-red needles (from dilute alcohol).

Reactions.—1. Potash-fusion gives diphenyl *om*-dicarboxylic acid.—2. Yields diphenylene ketone on distillation.—3. Distillation with zinc-dust gives diphenylene-methane (fluorene).

Salts.— BaA' , 4aq.— CaA' , 2aq.— AgA' .

Diphenylene ketone carboxylic acid. [above 275°]. Formed by heating the dicarboxylic acid (Bamberger a. Hooker, *B.* 18, 1034; *A.* 229,

158). Pale yellow needles, sl. sol. alcohol. May be sublimed.— BaA' ,— AgA' : yellow pp.

Diphenylene ketone carboxylic acid

[1.2] $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{C}_6\text{H}_4\cdot\text{CO}_2\text{H}$ [1.5]. [227° cor.].

Formation (Graebe, *B.* 13, 1303; *B.* 20 845; *A.* 247, 275).—1. From diphenyl di-o-carboxylic acid by heating with H_2SO_4 at 120° or with POCl_3 or ZnCl_2 .—2. By heating diphenylene dicarboxylic acid with H_2SO_4 for 10 minutes at 150°.

Properties.—Yellow needles, v. sol. hot alcohol. Conc. H_2SO_4 forms a red solution.

Reactions.—1. Potash-fusion yields diphenyl di-o-carboxylic acid.—2. PCl_5 (1 mol.) forms $\text{C}_6\text{H}_4\langle\text{COCl}\rangle\text{C}_6\text{H}_4\langle\text{COCl}\rangle$ [128°], which may be crystallised from ligroin.—3. PCl_5 (2 pt.) at 160°

yields $\text{C}_6\text{H}_4\langle\text{COCl}\rangle\text{C}_6\text{H}_4\cdot\text{COCl}_2$ [95°], which yields fluorene carboxylic acid on reduction with zinc-dust and dilute acetic acid.—4. Zinc-dust and ammonia reduce it to $\text{C}_6\text{H}_4\langle\text{CO}_2\text{H}\rangle\text{CH}(\text{OH})$.—

5. HI and P give fluorene.—6. Phenol and SnCl_4 at 120° give $\text{C}_6\text{H}_4\langle\text{CO}_2\text{H}\rangle\text{C}(\text{C}_6\text{H}_5\text{OH})_2$ [165°], which yields AgA' and $\text{C}_{20}\text{H}_{14}\text{O}_2$ [p. 130°].—7. Resorcin gives risc, on heating, to $\text{C}_6\text{H}_4\langle\text{CO}_2\text{H}\rangle\text{C}(\text{C}_6\text{H}_5\text{OH})_2$, a yellowish-brown

powder which exhibits green fluorescence in alkaline solutions.

Salts.— $\text{NH}_4\text{A}'$ aq.— NaA' 6aq: yellow needles, v. sol. hot water.— AgA' : yellow pp.

Methyl ether MeA'. [132°]. Needles.

Ethyl ether EtA'. [103°]. Needles.

Chloride $\text{C}_{12}\text{H}_8\text{ClO}_2$. [128°].

Amide $\text{C}_{12}\text{H}_{10}(\text{NH}_2)_2$ [225°]. Silky yellow needles (containing $\frac{1}{2}\text{HOEt}$). Formed from the chloride, and also by heating phenanthraquinone monoxim with H_2SO_4 at 100° (Wegerhoff, *B.* 21, 2357).

Oxim $\text{C}_{12}\text{H}_{10}(\text{CO}_2\text{H})(\text{C:NOH})$. [263°].

Phenyl-hydrazide

$\text{C}_{12}\text{H}_8(\text{CO}_2\text{H})(\text{C:N}_2\text{HPh})$. [205°]. Brownish-yellow prisms, m. sol. alcohol.

Diphenylene ketone dicarboxylic acid

$\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ [1.3.6]. Formed by

oxidation of retene-quinone and of oxyisopropyl-diphenylene-ketone carboxylic acid (Bamberger a. Hooker, *B.* 18, 1033; *A.* 229, 151). Yellow needles (from HOAc). Not melted at 270°, but loses CO_2 at a higher temperature. Yields diphenyl on heating with CaO . Potash-fusion forms diphenyl tricarboxylic acid.— BaA'' .— AgA'' : yellow pp.

Methyl ether MeA''. [184°]. Yellow needles.

Ethyl ether EtA''. [115°]. Needles.

Oxim $\text{C}_{12}\text{H}_{10}(\text{CO}_2\text{H})_2\text{C:NOH}$. Yellow pp., not melted at 250°.

DIPHENYLENE KETONE OXIDE

$\text{CO}\langle\text{C}_6\text{H}_4\rangle\text{O}$. Xanthone. [174°]. (350°) at

730 mm. (Graebe, *A.* 254, 280). S. (alcohol) 7° in the cold; 8.5° at 78°.

Formation.—1. Obtained by oxidation of

$\text{CH}_2\langle\text{C}_6\text{H}_4\rangle\text{O}$ with CrO_3 and HOAc (Me z a.

Weith, *B.* 14, 192).—2. By the dry distillation of salicylide; the yield being 35 p.c. of the theoretical (Perkin, *B.* 16, 339).—3. By distilling phenyl phosphate with sodium *m*- or *p*-oxybenzoate (Richter).—4. By the action of POCl_3 on potassium-salicylate of ethyl.—5. By distilling neutral or basic sodium salicylate with P_2O_5 .—6. In small quantities, when salicylic acid is distilled.—7. By strongly heating sodium *o*-chlorobenzoate.—8. From sodium *o*-phenylbenzoate and POCl_3 .—9. To the amount of 12 p.c. of the theoretical quantity, by the action of *o*-chlorobenzoyl chloride on basic sodium salicylate.—10. By the action of conc. H_2SO_4 on $[\text{1:2}] \text{C}_6\text{H}_4(\text{OPh})\text{CO}_2\text{H}$ (Graebe, *B.* 31, 508).—11. By distilling phenyl salicylate (Seiffert, *J. pr.* [2] 31, 479).—12. By heating salicylic acid (1 mol.) with PCl_5 (1 mol.), then adding phenol and distilling (Klepl, *J. pr.* [2] 28, 217).—13. By distilling calcium *p*-oxybenzoate (Goldschmidt, *M.* 4, 128).—14. A product of the electrolysis of a solution of phenol in KOH aq at 260° (Bamberger a. Berle, *B.* 24, 3212).

Preparation.—1. Phenyl phosphate (20 g.) and sodic salicylate (20 g.) are distilled together; a violent action ensues; when it is over the residue is distilled over at 400° best in a current of air. The crude product is shaken with solution of NaOH and distilled with steam. The residue is extracted with alcohol, from which, on cooling, the ketone crystallises (R. Richter, *J. pr.* [2] 28, 276).—2. By distilling salicylic acid with Ac_2O , the salicylide which is first formed splitting off CO , when the temperature rises (Perkin, *C. J.* 43, 35). In this process there is formed a by-product $\text{C}_{12}\text{H}_8\text{O}_2$ [192°] which is converted by boiling alcoholic potash into an acid $\text{C}_{12}\text{H}_8\text{O}_4$ [276°] (A. G. Perkin, *C. J.* 43, 187).

Properties.—Long white needles, grouped concentrically. M. sol. ether, alcohol and benzoline, more sol. benzene and chloroform, insol. water. The solution in conc. H_2SO_4 shows blue fluorescence (Graebe, *B.* 15, 1679). Does not react with hydroxylamine or phenyl-hydrazine (Spiegler, *B.* 17, 808).

Reactions.—1. Reduced by zinc-dust or by HI to $\text{CH}_2\langle\text{C}_6\text{H}_4\rangle\text{O}$ [100-5°] but no further.—2. Potash-fusion converts it into salicylic acid and phenol.—3. If the fusion be stopped when the mass is pasty (at about 200°), dissolved in water and ppd. by HCl, di-oxy-benzophenone is obtained, $\text{CO}(\text{C}_6\text{H}_4\text{O})_2$.—4. Sodium-amalgam reduces the di-phenylene-ketone oxide (in dilute alcoholic solution) to $\text{C}_6\text{H}_5\text{O}_2$ [200°]. This body crystallises from CHCl_3 in prisms. It is split up by chromic acid into di-phenylene-ketone oxide and diphenylene methane oxide, so that it is perhaps a molecular compound of these two bodies.—5. Bromine at 200° forms a dibromo-derivative [212°].—6. Fuming H_2SO_4 gives a disulphonic acid which forms BaA'' aq, crystallising from hot water in needles (A. G. Perkin, *C. J.* 43, 192).

Isomeride $\text{C}_{12}\text{H}_8\text{O}_2$. [91°] (R.); [96°] (G.). A product of the action of POCl_3 on sodium salicylate (Richter, *J. pr.* [2] 28, 294). Formed also by heating the sulphate of *o*-diazobenzoic acid with phenol (Griess, *D.* 21, 981). Needles, v. e. sol. ether. Yields diphenyl on distillation

with zinc-dust. Br gives $\text{C}_{12}\text{H}_8\text{Br}_2$ [198°]. H_2SO_4 yields a disulphonic acid, which gives BaA'' aq crystallising in needles.

Dizanthone $\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{C}_6\text{H}_4\langle\text{CO}\rangle\text{C}_6\text{H}_4$. [256°]. Occurs in the product of the action of salicylic acid on resorcin (Kostanekci a. Seidmann, *B.* 25, 1654). It crystallises from HOAc in groups of needles, and its solution in H_2SO_4 shows greenish fluorescence.

References.—DI-AMIDO-, NITRO-, and OXY-DIPHENYLENE KETONE OXIDE.

PHENYLENE MERCAPTAN v. DI-THIO-RESORCIN AND DI-THIO-HYDROQUINONE.

Diphenylene mercaptan $\text{C}_6\text{H}_4(\text{SH})\text{C}_6\text{H}_4(\text{SH})$. [176°]. Formed by diazotising benzidine, and treating the product with potassium xanthate and alcoholic potash successively (Leuckart, *J. pr.* [2] 41, 212; cf. Gabriel, *B.* 13, 339). White plates (from alcohol).

Di-methyl ether MeA'' . [184°]. Plates.

Di-ethyl ether EtA'' . [135°]. Plates.

DI-DIPHENYLENE-METHANE v. FLUOR-

ENE.

(?) - **Diphenylene - methane** $\text{CH}_2\langle\text{C}_6\text{H}_4\rangle\text{CH}_2$. **Methylene-diphenyl**. [118°]. (295° uncorr.). V.D. 84 (calc. 83). Occurs, together with the (8)-isomeride, among the products of the passage of a mixture of benzene and toluene through a red-hot tube (Carnelley, *C. J.* 37, 708). Pearly plates (from alcohol), sl. sol. cold alcohol, v. sol. ether. Its alcoholic solution shows faint blue fluorescence. CrO_3 and HOAc oxidise it to $\text{C}_{12}\text{H}_8\text{O}_2$ [281° corr.]. Bromine in ether gives $\text{C}_{12}\text{H}_8\text{Br}_2$ [163°]. Picric acid forms a compound $\text{C}_{12}\text{H}_{10}\text{C}_6\text{H}_3\text{N}_3\text{O}$, crystallising in blood-red needles [81°].

(8)-**Diphenylene-methane** $\text{C}_{12}\text{H}_{10}$. [205°]. (320°). V.D. 86.2 (calc. 83). Formed as above. Pearly plates (from alcohol). Oxidised by CrO_3 in HOAc to $\text{C}_{12}\text{H}_8\text{O}_2$ [288° corr.] which sublimes in white needles.

DIPHENYLENE-METHANE OXIDE

$\text{CH}_2\langle\text{C}_6\text{H}_4\rangle\text{O}$ [100°]. (315° corr.). Formed, to the amount of 2 p.c., in the preparation of Ph₂O by heating phenol with AlCl_3 (Merz a. Weith, *B.* 14, 191). Formed also from diphenylene ketone oxide by heating with fuming HIAq at 160° or by distilling with zinc-dust (R. Richter, *J. pr.* [2] 28, 280; Graebe, *A.* 254, 282); and by distilling euxanthone over heated zinc-dust (Wichelhaus a. Salzmänn, *B.* 10, 1399; Graebe a. Ebrard, *B.* 15, 1678). White plates (from alcohol).

Reactions.—1. Oxidised by CrO_3 or fume HNO_3 to diphenylene ketone oxide.—2. PCl_5 forms HCl and a product whence water at 0° produces $\text{C}_{12}\text{H}_8\text{O}_4\text{PO}(\text{OH})_2$ [255°-260°] an acid forming AgA'' and $(\text{NH}_4)\text{A}''$.—3. Br forms $\text{C}_{12}\text{H}_8\text{Br}_2\text{O}$ and $\text{C}_{12}\text{H}_8\text{Br}_2\text{O}$ [136°].

DIPHENYLENE - METHANE SULPHIDE

$\text{CH}_2\langle\text{C}_6\text{H}_4\rangle\text{S}$. [128°]. (342°). Formed by reducing $\text{CO}\langle\text{C}_6\text{H}_4\rangle\text{S}$ with HI and P at 170° ; and also by passing phenyltolyl sulphide through a red-hot tube (Graebe a. Schultess, *A.* 263, 12). Needles, sl. sol. cold alcohol, v. e. sol. CHCl_3 .

DIPHENYLENE-METHANE SULPHONE
 $\text{CH}_3\langle\text{C}_6\text{H}_4\rangle\text{SO}_2$. [170°]. Formed by heating
 $\text{CO}\langle\text{C}_6\text{H}_4\rangle\text{SO}_2$ with HI and P at 170° (Graebe
 a. Schultess, A. 263, 15). Needles, v. sol. hot
 alcohol.

PHENYLENE-METHENYL-AMIDINE
 $\text{C}_6\text{H}_5\langle\text{NH}\rangle\text{CH}$. [167°]. (above 360°). Formed
 by boiling phenylene-o-diamine with formic
 acid (Wundt, B. 11, 826; Fischer, B. 22, 445).
 Trimetric crystals (from alcohol).—B'HCl aq.—
 B'HAuCl₃. Yields on methylation $\text{C}_6\text{H}_4\text{N}_2$ [33°]
 (278° at 730 mm.).

Carboxylic acid $\text{CO}_2\text{H.C}_6\text{H}_4\langle\text{NH}\rangle\text{CH}$.
 Formed by reducing the formyl derivative of
 (2,1,4)-nitro-amido-benzoic acid (Zehra, B. 23,
 3634). White needles, blackening without
 fusion when heated.—H₂SO₄: white needles.

m-Phenylene-methyl-diamine
 [1:3] $\text{C}_6\text{H}_4(\text{NH}_2)(\text{NHMe})$. *Methyl-phenylene*
diamine. *Amido-methyl-aniline* (265°–270°
 uncor.). Formed by reduction of m-nitro-
 methyl-aniline (Nöling a. Stricker, B. 19, 548).
 Oil. Gives a methyl-chrysoidine with diazo-
 benzene chloride.

p-Phenylene-methyl-diamine
 [1:4] $\text{C}_6\text{H}_4(\text{NH}_2)(\text{NHMe})$. (258° uncor.). Formed
 by reduction of p-nitroso-methyl-aniline (Fischer,
 B. 19, 2992) or of $\text{C}_6\text{H}_4(\text{NHMe})\text{N}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$
 (Bernthsen a. Goske, B. 20, 929). Oil, v. sol.
 water. FeCl₃ gives a red colour, which on suc-
 cessive treatment with HCl and H₂S becomes
 blue (dimethylthionine).—B'H₂SO₄: white
 needles (from water).

m-Phenylene-di-methyl-diamine
 [1:3] $\text{C}_6\text{H}_4(\text{NHMe})_2$. (269°) at 740 mm.
 S.G. 1.0995 (Goll, B. 13, 200); (258°) (Staedel
 a. Bauer, B. 19, 1915). * Formed by reduction of
 m-nitro-di-methyl-aniline. Oil. With nitrous
 acid it yields a colouring-matter closely resem-
 bling Bismarck brown. With diazobenzene
 chloride it yields a di-methyl-chrysoidine which
 dyes a somewhat redder shade than chrysoidine.
 PbO₂ and aqueous HOAc gives a yellowish-
 brown colour (Lauth, C. R. 11, 975).—B'HCl.
Acetyl derivative $\text{C}_6\text{H}_4(\text{NMe}_2)(\text{NHAc})$.
 [87°].

p-Phenylene-di-methyl-diamine
 [1:4] $\text{C}_6\text{H}_4(\text{NHMe})_2$. [41°]. (257° i.v.).
 Prepared by reduction of nitroso-di-methyl
 aniline and of $(\text{C}_6\text{H}_4\text{NMe}_2)_2\text{O}$ by tin and HCl
 (Schraube, B. 8, 616; Wurster, B. 12, 522;
 Weber, B. 10, 760). Prepared also by reduction
 of $\text{C}_6\text{H}_4(\text{NHMe})\text{N}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$ (E. Fischer, B. 16,
 2255). Formed also together with di-chloro-p-
 phenylene-diamine and di-chloro-p-phenylene-
 diamine by boiling nitroso-di-methyl-
 aniline with HCl (S.G. 1.2) (Möhlau, B. 19,
 2010).

Properties.—Long white needles or short
 prisms, v. sol. water, alcohol, and ether. PbO₂
 and aqueous HOAc give a magenta-red solution
 changing to violet-black (Lauth, C. R. 11, 975).
 Colours wood, and paper made from wood,
 crimson (Wurster, B. 20, 808).

Reactions.—1. Yields quinone on oxidation
 with MnO₂ and H₂SO₄.—2. Bromine in HOAc
 forms $\text{C}_6\text{H}_4\text{N}_2\text{Br}$, which crystallises from its red

alcoholic solution in green scales [146°]
 (Wurster a. Sendtner, B. 12, 1803).—3. H₂S
 and an oxidising agent (e.g. FeCl₃) gives
 methylene-blue (v. vol. iii. p. 265). Methylene-
 red $\text{S}_2\langle\text{N}\rangle\text{NMe}_2\text{Cl}$ is a by-product
 (Bernthsen, A. 230, 187; 251, 1).—4. Na₂S₂O₈
 and CrO₃ give $\text{C}_6\text{H}_4(\text{NMe}_2)(\text{NH}_2)\text{S}_2\text{O}_8\text{H}$, which
 yields methylene-blue on further oxidation.
 5. Aldehydes and ketones form products of con-
 densation, e.g. $\text{C}_6\text{H}_4(\text{NMe}_2)\text{N}:\text{CHPh}$ [93°] (Calm,
 B. 17, 2936), $\text{C}_6\text{H}_4(\text{NMe}_2)\text{N}:\text{CHC}_6\text{H}_4\text{OH}$ [1:2]
 [134°], and $\text{C}_6\text{H}_4(\text{NMe}_2)\text{N}:\text{CHC}_6\text{H}_4\text{OMe}$ [1:4]
 [148°] (Nuth, B. 18, 574; Steinhart, A. 241,
 346). Benzil and alcoholic KOH form
 $\text{CPhBzN}:\text{C}_6\text{H}_4\text{NMe}_2$ [139°]; benzoyl-acetone
 forms in like manner $\text{CH}_3\text{BzCMe}:\text{N}:\text{C}_6\text{H}_4\text{NMe}_2$
 [136°] (Vogtherr, Z. 25, 635). Benzoin gives
 $\text{CHPh(OH)CPh}:\text{N}:\text{C}_6\text{H}_4\text{NMe}_2$ [127°] on heating,
 while deoxybenzoin forms $\text{C}_2\text{H}_5\text{N}_2$ [139°].—
 6. Oxalic acid forms, on heating, the ether
 $\text{C}_6\text{H}_4(\text{NMe}_2)\text{NH.CO.CO}_2\text{Et}$ [117°] which yields
 a corresponding acid [192°] and amide [259°]
 (Sendtner, B. 12, 530).

Salts.—B'2HCl. Very deliquescent plates.
 —B'H₂SnCl₆. Cubes.—B'H₂PtCl₆.

Acetyl derivative $\text{C}_6\text{H}_4(\text{NMe}_2)(\text{NHAc})$.
 [130°]. (355°). Small leaflets or needles.

p-Phenylene-tri-methyl-diamine
 [1:4] $\text{C}_6\text{H}_4(\text{NMe}_2)(\text{NMeH})$. (265°). Obtained by
 reduction of its nitrosamine, which is formed by
 the action of nitrous acid on p-phenylene-tetra-
 methyl-diamine (Wurster a. Schobig, B. 12,
 1809). Oil.

Acetyl derivative. [95°]. Prisms.
Nitrosamine $\text{C}_6\text{H}_4(\text{NMe}_2)(\text{NMe.NO})$. [99°].
 Leaflets or tables, sl. sol. cold water.

m-Phenylene-tetra-methyl-diamine
 [1:3] $\text{C}_6\text{H}_4(\text{NMe}_2)_2$. [–2°]. (266° i.v.). S.G. 1.2
 992. Prepared by heating phenylene-m-diamine
 with methyl alcohol and HCl at 190° (Wurster
 a. Morley, B. 12, 1814). Purified by distilling
 with Ac₂O (Romburgh, R. T. C. 7, 2). Oil, sl.
 sol. water. HOAc and nitric acid give
 $\text{C}_6\text{H}_4(\text{NO}_2)_2\text{N}_2\text{Me}_2\text{NO}$ [132°]. s-Tri-nitro-benzene
 forms B'C₆H₃(NO₂)₃ [121°]. m-Di-nitro-benzene
 gives B'C₆H₃(NO₂)₂ [58°] crystallising in needles.
 Bromine forms oily $\text{C}_6\text{H}_3\text{Br}_2\text{N}_2\text{NaNO}_2$ and
 dilute HCl aq give oily $\text{C}_6\text{H}_3(\text{NO})_2\text{NMe}_2$, which
 forms a hydrochloride B'HCl, crystallising in
 dark-red needles (Witt, B. 18, 877).

Salts.—B'H₂Cl. 2aq: hygroscopic crystals.
 —B'H₂FeCy₄ aq. Pearly plates (Wurster a.
 Roser, B. 12, 1826).

Methyl iodide B'MeI. [192°]. Crystals,
 v. sol. water.—B'MeHI.

Di-methyl-o-di-iodide B'Me₂I₂. Plates,
 v. sol. water (Hofmann, Pr. 12, 639).

p-Phenylene-tetra-methyl-diamine
 [1:4] $\text{C}_6\text{H}_4(\text{NMe}_2)_2$. [51°]. (260° i.v.). Prepared
 by heating p-phenylene-di-methyl-diamine with
 MeOH and HCl aq at 200° (Wurster, B. 12, 526,
 1803, 1827). White leaflets, sl. sol. cold water,
 v. sol. alcohol. Its aqueous solution becomes
 violet-blue on exposure to air or addition of
 oxidising agents. The blue substance appears
 only to exist as a salt, e.g. $\text{C}_6\text{H}_4\langle\text{NMe}_2\text{Cl}\rangle\text{CH}_2$
 (Wurster, B. 19, 3195; 20, 256; 21, 921). It
 becomes colourless on further oxidation.

Reactions.—1. Bromine in HOAc forms a

blue colouring matter $C_{10}H_7N_3$, which forms blue solutions in water and alcohol.—2. K_2FeCy , added to a solution of the sulphate forms $C_{10}H_7N_2H.FeCy$, crystallising in lustrous blue needles.—3. Sodium nitrite and hydrochloric acid give $C_{10}H_7(NMe_2)(NMeNO)$ [98°] and $C_{10}H_7(NO_2)(NMe_2).NMe.NO$ [87°].

Salts.— $B'2HCl$; crystals.— $B'H.PtCl_4$.— $B'2H.SO_4$.— $B'H.FeCy$; white needles.

Methylo-iodides $B'MeI$. [above 270°]. Leaflets (W.).— $B'Me.L$. Plates (Hofmann).

Reference.—NITRO-PHENYLENE-DI-METHYL-DIAMINE.

PHENYLENE-DI-METHYL-DI-AMINE SULPHONIC ACID $C_6H_4(NH_2)(NMe_2).SO_3H$. Got by reduction of *p*-nitro-di-methyl-amido-benzene sulphonic acid (Miehler & Walder, *B.* 14, 2176). Large rhombohedra, v. sol. water.— BAA' .— CaA' ; plates.

***p*-PHENYLENE-DI-METHYL-DI-ETHYL-DIAMINE** $C_6H_4(NMe_2)(NEt_2)$. (263°). Formed from [1:4] $C_6H_4(NEt_2)(NH_2)$, $MeOH$, and $HClAq$ at 200° (Lippmann & Fleissner, *M.* 4, 791). Liquid. Coloured blue by oxidising agents.

Methylo-iodide $B'2MeI$. [218°]. Yields $B'Me.PtCl_4$, $B'Me.AuCl_3$, $B'Me.CdI_2$, and $B'Me.(C_2H_5N_2O_2)$, [235°].

***o*-PHENYLENE-METHYL-ETHYLENE-DIAMINE** $C_6H_4 \begin{smallmatrix} NMe \\ \diagup \diagdown \\ NH \end{smallmatrix} > C_6H_4$. *v*-Methyl-quin-

oxaline tetrahydride. (274°). Formed by heating phenylene-ethylene-diamine with MeI at 110° (Ris, *B.* 21, 381). Liquid. Its aqueous solution is coloured blue by $FeCl_3$.

Methylo-iodide $B'MeI$. [above 200°]. Crystals.— $B'Me.PtCl_4$. Yellow needles.

DIPHENYLENE-METHYL-FURFURANE $C_6H_4.O \begin{smallmatrix} CH \\ \diagup \diagdown \\ C.OH.CMe \end{smallmatrix}$ [124°]. Got by reducing $C_6H_4.C(OH).CH_3.Ac$ (Japp & Klingemann, *B.* 21, 2932).

PHENYLENE-DI-METHYL-DI-MALONIC ACIDS $C_6H_4(CH_2.CH(CO_2H))_2$. The ethers of these acids are formed by the action of zinc-dust on the acids $C_6H_4(CH_2.CCl(CO_2Et))_2$, which are formed from sodium chloro-malonic ether and *o*-di-bromo-xylenes (Perkin & Kipping, *C. J.* 53, 16; *B.* 19, 437; 21, 86). The *o*- and *m*-ethers are oily, the *p*-ether is crystalline [51°]. The ethers form deliquescent sodium derivatives $Na_2C_6H_4O_2$, and the *o*-compound of this formula is converted by iodine into the tetrahydride of naphthalene tetracarboxylic ether. The *m*-acid is a liquid v. sol. water, the *p*-acid is crystalline [195°]. The *p*-acid forms Ag_2A'' , and when heated splits up into CO_2 and $C_6H_4(CH_2.CH_2.CO_2H)_2$ [223°].

PHENYLENE-METHYL-METHENYL-AMIDINE $C_6H_4 \begin{smallmatrix} NMe \\ \diagup \diagdown \\ N \end{smallmatrix} > OH$. [38°]. (278°) at

780 mm. Formed from phenylene-methenyl-amidine, MeI , and $MeOH$ at 100° (O. Fischer, *B.* 23, 644). Prisms.— $B'H.AuCl_4$. Needles.

DIPHENYLENE-METHYL-PYRAZINE $C_6H_4.C:N.CMe$ $C_6H_4.C:N.CH$ [128°]. Formed from phenanthraquinone and propylene-diamine (Strache, *B.* 21, 3362). White needles.— $B'H.PtCl_4$.

***v*-p-DIPHENYLENE-TETRA-METHYL-DI-PYRROLE** $C_{10}H_{11}N_4$ i.e.

$CH.CMe > N.C_6H_4.C_6H_4.N < CMe.CH$ [180°].

Got by heating an alcoholic solution of acetyl-acetone (2 mols.) and benzidine (1 mol.) (Paal & Schneider, *B.* 19, 3158). Colourless tables. Sol. alcohol, ether, benzene, and ligroin.

DIPHENYLENE-METHYL-QUINOXALINE

$C_{10}H_7N_2$ i.e. $C_6H_5Me < \begin{smallmatrix} N.C.C_6H_4 \\ N.C.C_6H_4 \end{smallmatrix} >$ [213°]. Formed from (1,3,4)-tolylene-diamine and phenanthraquinone in $HOAc$ (Hinsberg, *B.* 17, 323). Yellow hair-like crystals, v. sol. benzene.

DIPHENYLENE-M-NAPHTHOQUINOXAL

INE $C_{10}H_7 < \begin{smallmatrix} N.C.C_6H_4 \\ N.C.C_6H_4 \end{smallmatrix} >$ [273°]. Formed by

boiling an alcoholic solution of (1,2)-naphthylene-diamine with phenanthraquinone in $HOAc$ (Lawson, *B.* 18, 2426). Small yellow crystals.

The sulphonic acid, got by mixing a hot aqueous solution of naphthylene-*o*-diamine sulphonic acid with phenanthraquinone dissolved in $NaHSO_4$ with addition of $NaOAc$, forms a yellow crystalline Na salt, sol. hot water, but ppd. by alkalis (Witt, *B.* 19, 1719, 2791). When fused with KOH it yields the insoluble γ -rhodol $C_6H_5 \begin{smallmatrix} N \\ \diagup \diagdown \\ N \end{smallmatrix} > C_{10}H_6(OH) \begin{smallmatrix} [14] \\ [24] \end{smallmatrix}$, which forms a scarlet hydrochloride.

***m*-PHENYLENE-DI-(β)-NAPHTHYL**

DIAMINE $C_6H_4(NHC_{10}H_7)_2$. [126°]. Formed by heating *m*-phenylene-diamine with (β)-naphthol (Ruhemann, *B.* 14, 2654). Felted needles, sol. alcohol and ether.

***p*-Phenylene-di-(β)-naphthyl-diamine**

$C_{10}H_7(NHC_{10}H_7)_2$. [235°]. (over 400° in vacuo). Formed by heating *p*-phenylene-diamine with (β)-naphthol at 200° (Ruhemann, *B.* 22, 1080). White plates, almost insol. boiling alcohol, v. sol. nitro-benzene. KNO_3 added to its solution in conc. H_2SO_4 gives a greenish-violet colour, changing to blue.— $B'2C_6H_5N_2O_2$. [c. 217°].

Acetyl derivative $C_6H_4(NAc.C_{10}H_7)_2$ [210°]. Plates (from benzene).

Benzoyl derivative $C_6H_4(Bz.N)_2$ [220°].

Reference.—NITRO-PHENYLENE-NAPHTHYL-DIAMINE.

PHENYLENE-NAPHTHYLENE-AMINE

$C_{10}H_{11}N$ i.e. $\begin{smallmatrix} (1:2) C_6H_4 \\ (2:3) C_{10}H_7 \end{smallmatrix} > NH$. Phenyl-naphthyl-carbazole. [330°]. (454°) (Schweizer, *A.* 264, 195). S. (alcohol) .25 at 78°; S. (toluene) .5 at 111° (Bechi, *B.* 12, 1978). Occurs in crude anthracene, from which it may be got from the residues after sublimation of the anthracene (Graebe & Knecht, *B.* 12, 341, 2242; *A.* 20, 1). Formed by passing phenyl-(β)-naphthyl-amine through a red-hot tube. Colourless plates, v. sl. sol. $HOAc$. Its solutions show blue fluorescence. Oxidation by K_2CrO_7 and H_2SO_4 forms the quinone $C_{10}H_6O_2 > NH$ [307°] which crystallises from $HOAc$ in reddish-yellow needles, and is accompanied by $C_6H_4.O >$ which crystallises from benzene in red prisms.

Acetyl derivative $C_{10}H_9NO$. [121°].

Nitrosamine $C_{10}H_9N.O$. [210°].

Tetrahydride $C_{10}H_{11}N$. Formed by

reduction with H_2Iq and P at 210° . Syrup.—B'HI. Long needles.

Phenylene-naphthylene-amine

[1:2] $\text{C}_6\text{H}_4 > \text{NH}$ [235°]. Formed by heating [2:1] $\text{C}_6\text{H}_4 > \text{NH}$ with reduced copper at 240° (Kym, B. 23, 2465). Greenish-yellow plates, sl. sol. cold benzene, v. sol. hot alcohol.

PHENYLENE-NAPHTHYLENE-KETONE

OXIDE $\text{CO} < \text{C}_6\text{H}_4 > \text{O}$. [155°]. Formed by boiling (a)-naphthylsalicylate (Graebe & Feer, B. 19, 2612). Formed also by heating (a)-naphthol with salicylic acid and HOAc ; and by distilling (1,2)-(a)-naphthol carboxylic acid with salicylic acid (Kostanecki, B. 25, 1643). Crystals, sl. sol. cold alcohol. Its solution in H_2SO_4 shows green fluorescence. Converted by potash-fusion into o-(a)-di-oxy-phenyl-naphthyl-ketone (Phomina, A. 257, 92).

Isomeride. [140°]. Formed in like manner from (b)-naphthyl salicylate; and by heating (2,1)-(b)-naphthol carboxylic acid with salicylic acid. Needles. Reduced by zinc-dust to $\text{CH}_2 < \text{C}_6\text{H}_4 > \text{O}$. [80°].

p-PHENYLENE-DI-(b)-NAPHTHYL-DI-METHYL-DIAMINE $\text{C}_6\text{H}_4(\text{NMe}_2)_2$. [180°]. Formed from $\text{C}_6\text{H}_4(\text{NHCO}_2\text{H})_2$, MeI, and MeOH at 140° (Rueff, B. 22, 1080). Plates.

PHENYLENE-NAPHTHYLENE OXIDE

$\text{C}_6\text{H}_4 > \text{O}$. [178°]. Formed by distilling a mixture of phenol and (a)-naphthol with PbO (Arx, B. 13, 1726; A. 209, 141). Yellow needles, sl. sol. alcohol. H_2SO_4 forms a tetrasulphonic acid which gives $\text{Ba}_2\text{C}_6\text{H}_4\text{S}_4\text{O}_{13}$ 4aq. CrO_3 and HOAc form $\text{C}_6\text{H}_4\text{S}_4\text{O}_{13}$ [140°].— $\text{C}_6\text{H}_4\text{O}_2\text{C}_6\text{H}_4\text{N}_2\text{O}$. [165°].

Isomeride $\text{C}_6\text{H}_4\text{O}$. [296°] (A.); [300°] (G. a. K.). Formed in like manner from (b)-naphthol (A.). Got also by distilling the compound $\text{C}_6\text{H}_4\text{O}_2$ (from phenylene-naphthylene-amine) with zinc-dust (Graebe & A. Knecht, A. 202, 15). Plates, v. sol. toluene.

References.—DI-BROMO-, DI-CHLORO-, and DI-NITRO-PHENYLENE-NAPHTHYLENE OXIDE.

PHENYLENE OXIDE $\text{C}_6\text{H}_4\text{O}$ [103°]. A product of the distillation of o-oxy-benzoyl-o-oxy-benzoic acid (Märker, A. 124, 249). Silky needles (from alcohol). HNO_3 yields the nitro-compound $\text{C}_6\text{H}_4(\text{NO}_2)\text{O}$ [160°].

Diphenylene oxide $\text{C}_{12}\text{H}_8\text{O}$ i.e. $\text{C}_6\text{H}_4 > \text{O}$. [87°]. (283°) (Galewsky, A. 264, 188).

Formation.—1. By distilling Ph_2PO over lime, MgO , or PbO (Lesimple, A. 138, 375; Hoffmeister, Z. [2] 7, 24; A. 159, 211; Kreysler, B. 18, 1720).—2. By distilling phenol (2 pts.) with PbO (3 pts.) (Behr & A. Dorp, B. 7, 398; Graebe, A. 174, 190).—3. By distilling Ca(OPh) (Niederhäusern, B. 15, 1120).—4. By the action of red-hot lime on di-phenylene-ketone oxide.—5. One of the products of the action of HCl on murex acid at 160° .

Properties.—White plates (from alcohol). Converted by AsCl_3 into $\text{CH}_3\text{CO} < \text{C}_6\text{H}_4 > \text{O}$ [81°], which yields an oxim [146°] and a phenyl-hydrazide [233°]. H_2SO_4 forms a deliquescent disulphonic acid, which yields $\text{BaC}_6\text{H}_4\text{S}_2\text{O}_7$ aq.

Picric acid compound $\text{C}_6\text{H}_4\text{O} \cdot \text{C}_6\text{H}_3\text{O}_3$. [24°]. Yellow crystals (Goldschmidt & Schmidt, M. 2, 14).

References.—AMIDO-, BROMO-, TETRA-CHLORO-, DI-iodo, DINITRO-PHENYLENE OXIDES.

o-PHENYLENE-OXY-BENZAMIDINE

$\text{C}_6\text{H}_3 < \text{NH} > \text{C}_6\text{H}_4\text{OH}$. [223°]. Formed by reducing salicyl-o-nitro-aniline with tin and HCl (Mensching, A. 210, 345). Needles.— B^1HCl aq.— $\text{B}^2\text{H}_2\text{SO}_4$ aq. Needles, sl. sol. Aq.

o-PHENYLENE-PHENYL-DIAMINE. The sulphonic acid which gives the barium salt BaA_2 2aq may be got from its anilide [1:2:1] $\text{C}_6\text{H}_3(\text{NHPh})(\text{NH}_2)\text{SO}_3\text{NHPh}$ [157°] which is got by reduction of $\text{C}_6\text{H}_3(\text{NHPh})(\text{NO}_2)\text{SO}_3\text{NHPh}$, and yields B^1HCl [182°] (Fischer, B. 24, 3794).

p-Phenylene-phenyl-diamine $\text{C}_6\text{H}_4(\text{NHPh})_2$. **Amido-diphenylamine**. [67°] and [76°]. [354°].

Formation.—1. By reduction of nitro-diphenylamine (Nietzki, A. Witt, B. 12, 1401). 2. From p-nitroso-diphenylamine by boiling with alcoholic potash, by reduction with tin and HCl (Ikuta, A. 243, 279), or by treatment with phenyl-hydrazine in ether (O. Fischer, B. 31, 2615).—3. Together with azophenine, by heating p-nitroso-diphenylamine with aniline and aniline hydrochloride (O. Fischer & Hepp, B. 20, 2480). 4. By reducing $\text{C}_6\text{H}_4(\text{NHPh})_2\text{N}_2\text{C}_6\text{H}_4\text{SO}_3\text{Na}$ (Hess & Bernthsen, B. 18, 692).

Properties.—Plates or needles, sl. sol. water, v. sol. alcohol. Melts at 75° after crystallisation from ligroin. FeCl_3 added to a solution of its salts gives a red colour, turned green by excess. Yields quinone on oxidation.

Salt.— $\text{B}^2\text{H}_2\text{SO}_4$. Plates.

Nitrosamine $\text{C}_6\text{H}_4\text{N}_2\text{O}$. [c. 130°].

Acetyl derivative $\text{C}_6\text{H}_4\text{N}_2\text{O}$. [158°].

Benzoyl derivative (Lollmann, B. 15, 826).

Sulphonic acid.

[1:2] $\text{C}_6\text{H}_3(\text{NHPh})(\text{NH}_2)\text{SO}_3\text{H}$. Formed by reducing $\text{C}_6\text{H}_3(\text{NHPh})(\text{NO}_2)\text{SO}_3\text{H}$ (Fischer, B. 24, 3800). Yields BaA_2 aq and an anilide [171°], which gives B^1HCl [215°].

m-Phenylene-di-phenyl-diamine

$\text{C}_6\text{H}_3(\text{NHPh})_2$ [95°]. Formed by heating resorcin (2 mols.) with aniline (8 mols.), CaCl_2 (8 mols.) and ZnCl_2 (1 mol.) for 35 hours at 210° (Calm, B. 16, 2792). Flat needles, v. sol. ether. Oxidising agents give a green colour passing to bluish violet. Amyl nitrite and alcohol HCl form the p-nitroso-derivative $\text{C}_6\text{H}_3\text{N}_2\text{O}$, crystallising in brown-red prisms and yielding B^2HCl (Fischer & Hepp, A. 255, 145). B^2HCl : needles decomposed by water.

Acetyl derivative $\text{C}_6\text{H}_3(\text{NPhAc})_2$. [163°].

Benzoyl derivative $\text{C}_6\text{H}_3(\text{NPhBz})_2$. [184°].

Nitrosamine $\text{C}_6\text{H}_3(\text{NPhNO})_2$. [102°]. Yellow needles, forming a violet solution in H_2SO_4 .

p-Phenylene-di-phenyl-diamine

$\text{C}_6\text{H}_4(\text{NHPh})_2$. [132°] (Bandrowski, M. 8, 476); [141°] (Limpricht, B. 22, 2910); [145°] (O. Fischer, B. 21, 2615); [152°] (Calm, B. 16, 2803). Formed by heating hydroquinone (5 pts.) with aniline (17 pts.), CaCl_2 (20 g.), and ZnCl_2 (5 g.) for 18 hours at 210° . Formed also by the action of phenyl-hydrazine on nitroso-diphenyl-

DIPHENYLENE-PYRAZINE. Dihydrate

$C_{12}H_{10}N_2$, i.e. $C_6H_5.C_6H_4.N_2$. Formed from phenanthraquinone and ethylene-diamine (Mason, *B.* 19, 112; 20, 267). — $B'H.PtCl_4$.

(a)-PHENYLENE- β -STYRYL-KETONE

$C_{15}H_{12}O$, $\begin{smallmatrix} CO.C_6H_4.CH \\ | \\ C-N:CH \end{smallmatrix}$ [141°]. Formed by distilling the dicarboxylic acid

$C_6H_5O < \begin{smallmatrix} C(CO_2H):CH \\ C:N : C(CO_2H) \end{smallmatrix} >$ [284°], which is formed by oxidising (a)-styryl-(β)-naphthoquinoline carboxylic acid (Doebner a. Peters, *B.* 23, 1241). Yields a *picric acid compound* [197°]. The dicarboxylic acid yields Ag_2A'' .

(β)-Phenylene-pyridyl-ketone

$C_{15}H_{12}O$, $\begin{smallmatrix} CO.C_6H_4.N:CH \\ | \\ C-CH:CH \end{smallmatrix}$ [129°]. Formed in like manner from the corresponding dicarboxylic acid [264°] which is got by oxidising (a)-styryl-(a)-naphthoquinoline carboxylic acid with $KMnO_4$. Needles. Yields $B'H.PtCl_4$ 2a. The dicarboxylic acid forms Ag_2A'' as a pp.

PHENYLENE-QUINOLYNE KETONE

Oxide $C_{18}H_{12}NO_2$, i.e. $O < \begin{smallmatrix} C_6H_4 \\ C_6H_4 \end{smallmatrix} > CO$. *Phenoguinanthone*. [188°]. Formed by distilling *p*-oxy-quinoline with salicylic acid. Needles (from alcohol). — $B'HCl$: needles.

DIPHENYLENE-QUINOXALINE $C_{20}H_{12}N_2$

i.e. $C_6H_5.C_6H_4.N < C_6H_4.N > C_6H_5$. [217°]. Got from phenylene-diamine and phenanthraquinone (Hinsberg, *A.* 237, 340). V. sl. sol. alcohol.

DIPHENYLENE-STYRYL-OXAZOLE

$C_{17}H_{12}O$, $\begin{smallmatrix} C_6H_5.C_6H_4.O \\ | \\ C.C_6H_4.CHPh \end{smallmatrix}$ [172°]. Formed from phenanthraquinone, cinnamic aldehyde, and alcoholic NH_3 at 100° (Wadsworth, *C. J.* 57, 11). •Yellow needles.

p-PHENYLENE-DISULPHIDE $C_{12}H_8S_2$

Formed by oxidising dithiohydroquinone with an alkaline ferricyanide solution (Lenekart, *J. pr.* [2] 41, 206). Chars without melting at 300°, in sol. ordinary solvents. Is reduced by fusing with potash to dithiohydroquinone.

Diphenylene sulphide $\begin{smallmatrix} C_6H_5 \\ | \\ C_6H_4 \\ | \\ C_6H_5 \end{smallmatrix} S$. [97°]. (333° i.v.). Formed by passing Ph_2S through a red-hot tube (Stenhouse, *A.* 156, 332; Graebe, *A.* 174, 185). Needles, m. sol. alcohol. Yields on oxidation the sulphone $C_{12}H_8SO_2$ [230°].

Diphenylene - disulphide $C_6H_5 < \begin{smallmatrix} S \\ S \end{smallmatrix} > C_6H_5$ [154°]. (366°). A product of the distillation of sodium benzene sulphonate (Stenhouse, *Pr.* 17, 62; *A.* 149, 252). Formed also by heating phenol with P_2S_5 (Graebe, *A.* 174, 185; 179, 178), by heating benzene with S and $AlCl_3$ at 80° (Friedel a. Crafts, *A. Ch.* [6] 1, 530; 14, 439), and by heating $C_6H_5 < \begin{smallmatrix} S \\ S \end{smallmatrix} > N$ (Jacobson a.

Elley, *B.* 29, 910). Prisms (from CS_2). Conc. H_2SO_4 forms a purple solution. CrO_3 in $HOAc$ gives the sulphone $C_{12}H_8S_2O_2$ [325°] and the sulphoxide $C_{12}H_8S_2O$ [241°], sl. sol. cold benzene. Br forms $C_{12}H_8S_2Br$, crystallising from CS_2 in small black prisms.

m-PHENYLENE SULPHOCYANIDE

$C_6H_4(SCN)$, [54°]. Formed by heating the lead salt of di-thio resorcin with ICy and

alcohol at 100° (Gabriel, *B.* 10, 184). Needles, v. s. sol. hot alcohol. Yields a nitro-compound $C_6H_4(NO_2)(SCN)$ [150°].

DIPHENYLENE SULPHONE v. DIPHENYLENE SULPHIDE.

DI-PHENYLENE SULPHONE KETONE

$C_6H_5 < \begin{smallmatrix} SO_2 \\ CO \end{smallmatrix} > C_6H_5$. [185°]. Formed by heating benzophenone with fuming H_2SO_4 (Beckmann, *B.* 6, 1112; 8, 992), and by oxidising $C_6H_5 < \begin{smallmatrix} S \\ CO \end{smallmatrix} > C_6H_5$ (Graebe a. Schultze, *A.* 263, 10). Yellowish needles, v. sol. alcohol.

PHENYLENE DITHIOCARBAMIC ETHERS

$C_6H_5(NH.CO.SE)$. Formed by boiling from phenylene-thiocarbimide with alcohol (Billeter a. Steiner, *B.* 20, 230). The *m*-compound [116°] and the *p*-compound [197°] are crystalline and yield Ag_2A'' as white pps.

PHENYLENE-DI-THIO-CARBIMIDE

$C_6H_5(NCS)_2$. Formed from phenylene-diamine and $CSCl_2$ (Billeter a. Steiner, *B.* 20, 231). The *o*-compound [50°], *m*-compound [53°] (250°), and *p*-compound [130°] all crystallise in needles. **m-PHENYLENE-DI-THIO-DIGLYCOLLIC ACID** $C_6H_4(SCH_2.CO_2H)_2$. [127°]. Formed from di-thio-resorcin and $ClCH_2.CO_2H$ (Gabriel *B.* 12, 1639). Microcrystalline powder.

Diphenylene-di-thio-di-glycollic Acid

$C_{12}H_8(S.CH_2.CO_2H)_2$. [252°]. Formed from $C_6H_5(SH)_2$, $NaOH$, and chloro-acetic acid (Gabriel, *B.* 13, 390).

o-PHENYLENE-THIO-UREA

$C_6H_5 < \begin{smallmatrix} NH \\ NH \end{smallmatrix} > CS$. [298°]. Formed by heating *o*-phenylene-diamine hydrochloride with ammonium sulphocyanide and water at 180° (Lellmann, *B.* 15, 2146; *A.* 221, 9). Formed also from *o*-phenylene-diamine and SCl_2 (Billeter a. Steiner, *B.* 20, 231). Plates (from dilute alcohol, sl. sol. water). The crystalline *m*-isomeride is got by heating *m*-phenylene-diamine with CS , and some alcohol at 150° (Gucci *G.* 17, 524). The *p*-isomeride melts at 271°.

Phenylene-di-thio-di-ureas

$C_6H_4(NH.CS.NH)_2$. *m*- [215°]. *p*- [220°] Formed by heating phenylene-diamine hydrochloride with ammonium sulphocyanide (Lellmann, *A.* 221, 11; *B.* 15, 2849). The *p*-compound is also formed from *p*-phenylene dithiocarbimide and alcoholic NH_3 (Billeter a. Steiner, *B.* 20, 230).

Diphenylene - thio - urea $\begin{smallmatrix} C_6H_5.NH \\ | \\ C_6H_4.NH \end{smallmatrix} > CS$

[238°]. Formed by heating di-*o*-amido-diphenyl with alcohol and CS_2 (Heuland, *C. J.* 58, 167; *B.* 22, 3014).

o-PHENYLENE-TOLENYL-AMIDINE

$C_6H_4.Me.C < \begin{smallmatrix} NH \\ N \end{smallmatrix} > C_6H_4$. [268°]. Formed from *o*-phenylene-diamine and *p*-toluic chloride, and also by reduction of *p*-toluyl-*o*-nitro-aniline (Hübner, *A.* 210, 328; cf. Brückner, *A.* 205, 115). Prisms (from alcohol). — $B'HCl$. — $B'H.PtCl_4$. — $B'HNO_2$. — $B'H_2SO_4$: slender needles.

PHENYLENE-DI-p-TOLYL-DIAMINE

$C_{22}H_{20}N_2$, i.e. $C_6H_4(NH.C_6H_4.Me)_2$. [187°]. Formed by heating resorcin with *p*-toluidine, $ZnCl_2$, and $CaCl_2$ (Hatschek a. Zega, *J. pr.* [2] 33, 218). Needles. Yields a di-nitrosamine $C_{22}H_{18}N_2O_2$ [c. 150°], a di-acetyl derivative

$C_6H_5Ac.N_2$ [176°], and a di-benzoyl derivative $C_6H_5Bz.N_2$ [152°].— B^*2HCl ; crystalline powder, decomposed by water.

Phenylene-di-o-tolyl-p-diamine [135°]. (420°). Formed by heating hydroquinone with o-toluidine and $CaCl_2$ at 290° (Philip, *J. pr.* [2] 34, 66). Plates (from $HOAc$). Yields a di-nitrosamine [140°]. Yields $C_6H_5Ac.N_2$ [235°] and $C_6H_5Ac.N_2$ [189°].— B^*2HCl : needles.

Phenylene-di-p-tolyl-p-diamine. [182°]. Formed by heating hydroquinone or phenyl-p-amido-phenol with p-toluidine and $ZnCl_2$ at 220° (H. a. Z.); Calm, B. 16, 2810). Plates. Yields a di-nitrosamine [152°], a di-acetyl derivative [173°], and a di-benzoyl derivative [222°].— B^*2HCl .

PHENYLENE-TOLYLENE-KETONE OXIDE

$C_6H_5 \begin{smallmatrix} CO \\ \diagup \diagdown \end{smallmatrix} C_6H_4Me$. Methyl-xanthone. [105°]. Formed by boiling p-tolyl salicylate (Graess a. Feer, B. 19, 2612; cf. Seifert, *J. pr.* [2] 31, 47°).

Isomeride $C_6H_5 \begin{smallmatrix} CO \\ \diagup \diagdown \end{smallmatrix} C_6H_4Me$ [176°]. Made by heating $C_6H_5Me(OH)CO_2Ph$ [19°] (Weber, B. 25, 1745). Crystals (from alcohol).

o-PHENYLENE-p-TOLYL-GUANIDINE

$C_6H_5 \begin{smallmatrix} NH \\ \diagup \diagdown \end{smallmatrix} C_6H_4Me$. [209°]. Formed by heating o-phenylene-diamine with di-p-tolyl-cyanamide at 210° (Keller, B. 24, 2509). Tables. Yields a mono-acetyl derivative [152°], a di-benzoyl derivative [191°], and a nitrosamine $C_6H_5(NO)N_2$ [150°-160°]. Phenyl cyanate forms

$C_6H_5 \begin{smallmatrix} CO \\ \diagup \diagdown \end{smallmatrix} N_2(C_6H_5):CNC_6H_4Me$ [254°] crystallising from benzene in small needles. Di-p-tolyl-cyanamide at 210° forms the compound $(NHC_6H_5)_2C:N_2(C_6H_5):C:N.C_6H_4Me$ [188°].

Salts.— B^*HCl .— $B^*H_2PbCl_4$.— $B^*H_2SO_4$.

DIPHENYLENE-TOLYL-METHANE $C_{20}H_{16}$

$C_6H_5 \begin{smallmatrix} CH \\ \diagup \diagdown \end{smallmatrix} CH.C_6H_4Me$. [128°]. Formed by the action of P_2O_5 on a mixture of diphenylene-carbinol and toluene, or of $AlCl_3$ on diphenylene-carbinyl chloride dissolved in toluene (Hemilian, B. 11, 208; *Bl.* [2] 34, 325). Silky needles.

PHENYLENE-DI-p-TOLYL-DI-METHYL-m-DIAMINE $C_6H_5 \begin{smallmatrix} NHMe \\ \diagup \diagdown \end{smallmatrix} NMe.C_6H_4Me$. (c. 400°). Got by heating phenylene-di-p-tolyl-m-diamine with MeI and KOH at 150° (Hatschek a. Zega, *J. pr.* [2] 33, 223). Liquid smelling like geraniums.

The isomeric phenylene-di-o-tolyl-di-methyl-p-diamine (385°-390°) and phenylene-di-p-tolyl-di-methyl-diamine [153°] may be prepared in like manner (Philip, *J. pr.* [2] 34, 57; H. a. Z.).

o-PHENYLENE-UREA $C_6H_5 \begin{smallmatrix} NH \\ \diagup \diagdown \end{smallmatrix} CO$

[308°]. Formed by heating o-amido-phenyl-carbamie ether at 90° (Rudolph, B. 12, 1296), by heating o-amido-di-phenyl-urea (Lellmann a. Würthner, A. 228, 220), by heating its ethyl derivative with HCl (Sandmeyer, B. 19, 2654), and by the action of $COCl_2$ in toluene on a solution of o-phenylene-diamine hydrochloride at 100° (Hartmann, B. 23, 1046). Leaflets, sl. sol. water.— B^*HCl . Decomposed by water.

Ethyl derivative $C_6H_5 \begin{smallmatrix} NH \\ \diagup \diagdown \end{smallmatrix} C.OEt$. [160°]. Formed from o-phenylene-diamine and $NH_2C(OEt)_2$. Plates.

m-Phenylene-urea. [above 300°]. Formed by similar methods (Michler a. Zimmermann, B. 14, 2177; L. a. W.). Insoluble powder. ^o
p-Phenylene-urea. [above 320°]. Got by heating p-amido-di-phenyl-urea (L. a. W.).

Isomeride. [130°]. Got by boiling an alcoholic solution of oxy-phenyl-thio-urea with HgO (Bendix, B. 11, 2264). Tables, sol. water.

Phenylene-di-ureas $C_6H_5 \begin{smallmatrix} NH.CO.NH_2 \\ \diagup \diagdown \end{smallmatrix}$. o- [290°]. m- [above 300°]. Formed from phenylene-diamine hydrochloride and potassium cyanate in cold aqueous solutions (Warder, B. 8, 1180; Lellmann, A. 221, 13; B. 16, 592).

The p-compound can be heated to carbonisation without melting.

References.—AMIDO- and NITRO-PHENYLENE-UREA.

PHENYL-ENNOIC ACID.

Nitrile $C_6H_5 \begin{smallmatrix} CH(C_6H_5).CN \\ \diagup \diagdown \end{smallmatrix}$. (327°). Formed from $CH_3Ph.CN$, heptyl iodide, and $NaOH$ (Rosolymot B. 22, 1237). Yellow oil.

DI-PHENYL-ENNYL TRIANIDE

$C_6H_5.C_6H_4.N_3$. [c. 388°]. (c. 293° at 15 mm.). Formed from decolic chloride, benzotrile, and $AlCl_3$ (Krafft a. Koenig, B. 23, 2384).

PHENYL-ENNYL-THIO-UREA $C_6H_5 \begin{smallmatrix} NH.CO.NH_2 \\ \diagup \diagdown \end{smallmatrix}$. $NHPh.CS.NHC_6H_5$. [60°]. Formed from ennyl-thiocarbamide and aniline (Freund a. Schönfeld, B. 24, 3359). Tables, v. sol. alcohol and ligroin.

PHENYL-ENNYL-UREA $C_6H_5 \begin{smallmatrix} NH.CO.NH_2 \\ \diagup \diagdown \end{smallmatrix}$. $NHPh.CO.NHC_6H_5$. [63°]. Formed from phenyl cyanate and aniline in alcohol (Freund a. Schönfeld, B. 24, 3358). Long prisms.

s-DI-PHENYL-ETHANE $C_{14}H_{12}$

$CH_3Ph.CH_3Ph$. Dibenzyl. Mol. w. 182. [53°]. (277°). S.V.S. 174-2 (Schiff, A. 223, 261). H.F. - 31,200. H.C.v. 1,823,300. H.C.p. 1,830,200 (Berthelot a. Vieille, *Bl.* [2] 47, 866).

Formation.—1. By the action of Na on benzyl chloride (Cannizzaro a. Rossi, A. 121, 250; Fittig, A. 137, 257).—2. From ethylene chloride, benzene, and $AlCl_3$ (Silva, C. R. 89, 606; A. Ph. S. 18, 345).—3. From $CHBr:CHBr$, benzene, and $AlCl_3$ (Anschütz, A. 235, 152).—4. From acetylene, benzene, and $AlCl_3$ (Varet a. Vienne, *Bl.* [2] 47, 919).—5. By heating benzyl chloride with copper powder (Onufrovitch, B. 17, 833).—6. A product of the action of Na on o-bromo-benzyl-bromide (Jackson a. White, *Am.* 2, 390).—7. By adding sodium (70 g.) to an alcoholic solution of phenyl-cinnamionitrile (Freund a. Renise, B. 23, 2859).

Properties.—Long colourless needles, sol. alcohol, ether, and CS_2 .

Reactions.—1. Yields toluene and di-phenyl-ethylene when passed through a red-hot tube (Otto, Z. [2] 6, 22; A. 154, 176; Barbier, C. R. 78, 1769).—2. Chlorine passed into fused s-di-phenyl-ethane forms first $CHPh:CHPh$ and then $C_6H_5 \begin{smallmatrix} CH:CH \\ \diagup \diagdown \end{smallmatrix} C_6H_5$ (Kade, *J. pr.* [2] 19, 466). In presence of I , chlorine forms p-di-chloro-di-phenyl-ethane in the cold. Exhaustive chlorination yields C_6Cl_5 and C_6Cl_4 (Merz a. Weith, B. 16, 2877).—3. H_2SO_4 forms a disulphonic acid $C_6H_5 \begin{smallmatrix} (SO_3H)_2 \\ \diagup \diagdown \end{smallmatrix}$, which yields K^+A^- 2aq, Ba^+A^- 3aq, and Pb^+A^- 4aq (Kade, B. 6, 953). A tetra-sulphonic acid, $C_6H_5 \begin{smallmatrix} (SO_3H)_4 \\ \diagup \diagdown \end{smallmatrix}$, 3aq, is also formed.

s-Di-phenyl-ethane $CH_3.CHPh_2$. (270°) (O.); (286°) (H.).

Formation.—1. From CCl_4 , $CHPh_2$, alcohol,

and Na (Goldschmidt, *B. 6*, 1501).—2. From $\text{CH}_3\text{Ph.CH}_2\text{Br}$, benzene, and zinc-dust (Radziszewski, *B. 7*, 140).—3. From paraldehyde, benzene, and H_2SO_4 (Baeyer, *B. 7*, 1190).—4. Together with ethyl-benzene and di-methyl-anthracene dihydride by heating ethylidene chloride with benzene and AlCl_3 (Silva, *Bl. 2* 41, 418; Anschütz, *B. 17*, 165).—5. By distilling its dicarboxylic acid (Haiss, *B. 15*, 1481).

Properties.—Oil, with blue fluorescence. Solidifies in a freezing mixture. Yields benzophenone on oxidation. Fuming HNO_3 added to its solution in HOAc forms benzophenone, $\text{C}_6\text{H}_5(\text{OH}).\text{CH}_2.\text{O}.\text{NO}_2$ [107°], di-phenyl-vinyl nitrite (87°), and a body [148°] which yields di-phenyl-acetonitrile on reduction (Anschütz & Romig, *A. 233*, 329).

Tri-phenyl-ethane $\text{CH}_3\text{Ph.CHPh}_2$ (above 360°). Formed from $\text{CH}_3\text{Cl}.\text{CHCl}.\text{OEt}$, benzene, and AlCl_3 (Waas, *B. 15*, 1128). Liquid, with violet fluorescence. Insol. cold alc'hol.

s-Tetra-phenyl-ethane $\text{C}_{20}\text{H}_{16}$ i.e. $\text{CHPh}_2.\text{CHPh}_2$. Mol. w. 334. [210°]. S. (benzene) 14 at 80°. S. (95 p.c. alcohol) 8 on boiling.

Formation.—1. By distilling benzoyl and succinyl-di-phenyl-carbinol and by distilling di-phenyl-carbinol with succinic acid (Linnemann, *A. 133*, 24).—2. By distilling benzophenone with zinc-dust (Staedel, *B. 6*, 1401).—3. By reducing benzopinacol $\text{CPh}_2(\text{OH}).\text{CPh}_2(\text{OH})$ with HI and P (Graebe, *B. 8*, 1055).—4. From di-phenyl-carbinol, glacial HOAc , conc. HClAq , and zinc (Zagumenny, *A. 184*, 176; *Bl. 2* 34, 329).—5. By reducing (8)-benzopinacol $\text{CPh}_2.\text{CO}.\text{C}_6\text{H}_5$ with HI and P (Zincke & Thörner, *B. 11*, 67).—6. By boiling $(\text{CHPh}_2)_2\text{S}_2$ with alcohol and copper powder (Engler, *B. 11*, 926).—7. By reducing $\text{CPh}_2.\text{CPh}_2$ (Friedel & Balzoin, *Bl. 2* 33, 388).—8. From $\text{CHPh}_2.\text{Cl}$ and Na (Engler).—9. By the action of benzene and AlCl_3 on $\text{CBr}_2.\text{CH}_2.\text{Br}$, on $\text{CHBr}_2.\text{CHBr}_2$, on $\text{CPhIIBr}.\text{CHBr}_2$, on $\text{CPhBr}.\text{CPhBr}$, and on $\text{CHPhBr}.\text{CHPhBr}$, the yield in the last case being excellent (Anschütz, *A. 245*, 176).—10. By distilling CPh_2HCl (Anschütz, *A. 235*, 220).

Properties.—Needles (by sublimation), sl. sol. alcohol. Crystallises from benzene with C_6H_6 . Yields a crystalline tetra-nitro-derivative, a crystalline tetra-sulphonic acid, which gives Ba_2A^{IV} and $\text{C}_8\text{H}_8(\text{OH})_4$ [248°].

u-Tetra-phenyl-ethane $\text{CPh}_2.\text{CH}_2.\text{Ph}$ [140°]. Formed from CPh_2K and benzyl chloride (Hanriot, *C. R.* 108, 1119).

References.—AMIDO-, BROMO-, BROMO-AMIDO-, DI-BROMO-DI-NITRO-, CHLORO-, PENTA-CHLORO-DI-NITRO-, NITRO-, AND OXY-, PHENYL-ETHANES.

PHENYL-ETHANE DICARBOXYLIC ACID
v. CARBOXY-PHENYL-PROPIONIC ACID and PHENYL-SUCCINIC ACID.

Phenyl-ethane tricarboxylic acid $\text{CHPh}(\text{CO}_2\text{H}).\text{CH}(\text{CO}_2\text{H})_2$ [171°]. Got by saponifying its ether, which is made by the action of α -chloro- or α -bromo-phenyl-acetic ether on sodium malonic ether (Spiegel, *A. 219*, 31; Alexander, *A. 258*, 71). Small tablets, v. sol. hot water. Decomposed on fusion into CO_2 and phenyl-succinic acid. **Salts.**— $\text{Ca}_2\text{A}^{III}$, 10aq. $\text{Ca}_2\text{A}^{III}$, 5aq. ppd. from aqueous solution by alcohol— $\text{Ag}_2\text{A}^{III}$; crystalline pp.

Ethyl ether Et.A^{III} . [46°]. (202° at 10 mm.). Needles (from dilute alcohol).

Di-phenyl-ethane α -carboxylic acid $\text{C}_{16}\text{H}_{12}\text{O}_3$ i.e. $\text{C}_6\text{H}_5.\text{CH}_2.\text{CH}_2.\text{C}_6\text{H}_4.\text{CO}_2\text{H}$ [131°]. Formed by the action of HI and P at 200° on isobenzylidene-phthalide, and on deoxybenzoin carboxylic acid (Gabriel, *B. 11*, 1019; 18, 2440). Tablets (from dilute alcohol).— AgA^{IV} : pp.

Isomerides v. DI-PHENYL-PROPIONIC ACID.

Dj-phenyl-ethane di- α -carboxylic acid $\text{C}_{16}\text{H}_{12}\text{O}_6$ i.e. $\text{CO}_2\text{H}.\text{C}_6\text{H}_4.\text{CH}_2.\text{CH}_2.\text{C}_6\text{H}_4.\text{CO}_2\text{H}$. [186°] (H.). [229°] (D.).

Formation.—1. By heating diphthalyl with HI and P (Graebe, *B. 8*, 1055).—2. By the action of HI and phosphorus on the acid $\text{CO} < \text{C}_6\text{H}_4 > \text{CH}.\text{CH}_2.\text{C}_6\text{H}_4.\text{CO}_2\text{H}$ (Wislicenus, *B. 17*, 2181; Hasselbach, *A. 243*, 254), and on diphthalic acid (Dobref, *A. 239*, 66).

Properties.—Small needles, v. sol. alcohol and dilute HOAc . KMnO_4 in alkaline solution forms diphthalic acid [263°]. Distillation over soda-lime forms s-di-phenyl-ethylene.

Salts.— $(\text{NH}_4)_2\text{A}^{IV}$ (dried at 100°).— CaA^{IV} (at 100°).— BaA^{IV} .— $\text{Cu}_2\text{A}^{IV}\text{O}$.— $\text{Pb}_2\text{A}^{IV}\text{O}$.— $\text{Zn}_2\text{A}^{IV}\text{O}$.— AgHA^{IV} .

Methyl ether MeA^{IV} . [101°].

Ethyl ether Et.A^{IV} . [71°]. Converted by alcoholic NH_3 into the amio ether $\text{C}_6\text{H}_4(\text{C}_6\text{H}_4.\text{CO}_2\text{Et})(\text{C}_6\text{H}_4.\text{CONH}_2)$ [c. 67°].

Di-phenyl-ethane dicarboxylic acid $\text{C}_6\text{H}_5.\text{CH}_2.\text{CH}(\text{CO}_2\text{H}).\text{C}_6\text{H}_4.\text{CO}_2\text{H}$ [1:2]. [154°]. (above 300°). Formed by heating the nitrile

with conc. HCl at 220° (Eichelbaum, *B. 21*, 2682). Small prisms, sol. alcohol, insol. ether. **Nitrile** $\text{C}_6\text{H}_5.\text{CH}_2.\text{CH}(\text{CN}).\text{C}_6\text{H}_4.\text{CN}$ [110°]. (above 300°). Formed from benzyl chloride and [1:2] $\text{C}_6\text{H}_5(\text{CN}).\text{CH}_2.\text{CN}$. Plates, insol. water, alkalis, and acids.

Amide. [221°]. Formed by the action of conc. H_2SO_4 on the nitrile. Converted by conc. HCl (S.G. 1.19) at 100° into the imide $\text{C}_6\text{H}_5 < \text{CH}(\text{C}_6\text{H}_4) > \text{CO}$ [176°] (above 300°).

Di-phenyl-ethane di-carboxylic acid $\text{CH}_2.\text{CH}(\text{C}_6\text{H}_4.\text{CO}_2\text{H})_2$ [275°]. Got by heating the tri-carboxylic acid (Haiss, *B. 15*, 1481). Long needles. May be sublimed.— CaA^{IV} .

Isomeride v. DI-PHENYL-SUCCINIC ACID.

Di-phenyl-ethane tri-carboxylic acid $\text{CO}_2\text{H}.\text{CMc}(\text{C}_6\text{H}_4.\text{CO}_2\text{H})_2$ [255°]. Formed by oxidation of di- α -tolyl-propionic acid with KMnO_4 (Haiss, *B. 15*, 1479). Sol. alcohol and ether.— $\text{Ag}_2\text{HA}^{IV}$.— Ag_2A^{IV} .

Di-phenyl-ethane tri-carboxylic acid $\text{C}_6\text{H}_5.\text{O}_2$ i.e. $\text{CHPh}(\text{CO}_2\text{H}).\text{CPh}(\text{CO}_2\text{H})_2$. **Amide** $\text{CHPh}(\text{CO}_2\text{H}).\text{CPh}(\text{CONH}_2)_2$ [190°]. Got from $\text{CHPh}(\text{CO}_2\text{Et}).\text{CPh}(\text{CN})_2$. CO_2Et [105°] which is got by heating α -chloro-phenyl-acetic ether with alcoholic KCO_3 on a water-bath (Poppe, *B. 23*, 114).

Mono-nitrile $\text{CO}_2\text{H}.\text{CHPh}.\text{CPh}(\text{CN}).\text{CO}_2\text{H}$. The others MeA^{IV} [101°] and Et.A^{IV} (v. supra) are got from α -chloro-phenyl-acetic acid and KCO_3 in MeOH or EtOH . Conc. H_2SO_4 converts Et.A^{IV} into $\text{CO}_2\text{Et}.\text{CHPh}.\text{CPh}(\text{CO}_2\text{Et}).\text{CONH}_2$ [157°] crystallising in aggregates of needles.

References.—NITRO- and OXY- DI-PHENYL-ETHANE CARBOXYLIC ACID.

PHENYL-ETHENYL-AMIDINE v. **PHENYL-ACETAMIDINE**.**PHENYL-ETHENYL-AMIDO-PHENYL-MERCAPTAN** C_8H_7NS i.e.

$C_6H_5 \begin{smallmatrix} N \\ \diagup \diagdown \\ S \end{smallmatrix} C_6H_5$. Formed by heating phenyl-acetic chloride with *o*-amido-phenyl mercaptan (Hofmann, B. 13, 1234). Oil, sol. alcohol and ether. On fusion with potash it yields phenyl-acetic acid and amido-phenyl mercaptan. — B^*HCl . — $B^*H_2PtCl_6$ 5aq: needles.

PHENYL-ETHENYL-AMIDOXIM $C_8H_7N_2O$ i.e. $C_6H_5 \cdot CH_2 \cdot C(NOH) \cdot NH_2$. Phenyl-acetamidoxim. [67°]. Got by heating phenyl-acetonitrile with a solution of hydroxylamine in dilute alcohol (Knudson, B. 18, 468, 2482). Thin prisms, v. sol. water. Converted by phenyl cyanate into $C_6H_5 \cdot CH_2 \cdot C(NH \cdot CO \cdot NHPh) : NOH$. [123°]. — B^*HCl . [155°]. White prisms.

Acetyl derivative. [124°]. Plates.

Benzoyl derivative $C_8H_7C(=O)OBz \cdot NH_2$. [144°]. Prisms, v. sol. alcohol.

Ethyl ether $C_8H_7C(=O)OEt \cdot NH_2$. [58°]. Converted by potassium cyanate into $CH_3Ph \cdot C(=O)NH \cdot CO \cdot NHPh$ [148°].

Benzyl ether. [55°]. Prisms.

Phenyl-ethenyl-amidoxim

$CH_2 \cdot C(NOH) \cdot NHPh$. [121°]. Formed by heat-thioacetic anilide with hydroxylamine solution at 100° (Müller, B. 22, 2408; cf. Nordmann, B. 17, 2746). Satiny plates, v. sol. alcohol. $FeCl_3$ gives a violet colour, changing to olive green and, on heating, to red. — B^*HCl : needles. — $B^*H_2PtCl_6$: yellow needles.

Benzoyl derivative $C_8H_7C(=O)OBz \cdot NHPh$. [110°]. White needles (from dilute alcohol).

PHENYL-ETHENYL-AZOXIM v. **AZOXIMS**.

PHENYL-ETHENYL-DI-ETHYL-TRI-SULPHONE $CH_2 \cdot C(SO_2Et)_2(SO_2Ph)$. [109°]. Got by oxidation of $CH_2 \cdot C(SPh)(SO_2Et)_2$ (Laves, B. 25, 364). Needles, v. sol. alcohol.

TRI-PHENYL-ETHENYL-TRISULPHONE $CH_2 \cdot C(SO_2Ph)_3$. [182°]. Formed by the action of alcoholic $NaOH$ and MeI on $CH(SO_2Ph)_3$. Got also by oxidation of $CH_2 \cdot C(SPh)_3$ by $KMnO_4$ (Laves, B. 25, 352). Needles, v. sol. $CHCl_3$.

DI-PHENYL-ETHENYL-DI-UREA

$NHPh \cdot CO \cdot N : CMa \cdot NH \cdot CO \cdot NHPh$. [169°]. Formed by adding aqueous $NaOH$ (2 mols.) to an aqueous solution of acetamidine hydrochloride (2 mols.) shaken with phenyl cyanate (1 mol.) (Pinner, B. 23, 2923). Needles, m. sol. alcohol. Converted by boiling dilute (50 p.c.) acetic acid into acetyl-phenyl-urea [183°].

PHENYL ETHER v. **DI-PHENYL OXIDE**.

α -PHENYL-ETHYL ALCOHOL C_8H_9O i.e. $CH_3 \cdot CHPh \cdot OH$. Mol. w. 122. (203°). S.G. 1.013. Formed from $CH_3 \cdot CHBr \cdot C_6H_5$ by successive treatment with $AgOAc$ and $NaOH$ (Radziszewski, B. 7, 141; Berthelot, Z. 1868, 589). Got also by reducing acetophenone with sodium-amalgam (Emmerling a. Engler, B. 6, 1005). Yields an acetyl derivative C_8H_9OAc (217°–220°) which yields styrene on treatment with alcoholic potash.

Ethyl ether C_8H_9OEt . (186°). S.G. 22–931. Formed from $CH_3 \cdot CHBr \cdot C_6H_5$ and alcoholic NH_3 at 100° (Thorpe, Z. 1871, 131).

β -Phenyl-ethyl alcohol $CH_3 \cdot Ph \cdot CH_2 \cdot OH$. Benzyl-carbinol. (212°). S.G. 21–1034. Formed by reducing phenyl-acetic aldehyde with sodium-

amalgam (Radziszewski, B. 9, 373). Oil. As_2O at 150° converts it into an acetyl derivative C_8H_9OAc , (224°), S.G. 1.029.

PHENYL-ETHYL-ALLOPHANIC ETHER $C_{12}H_{15}N_3O$ i.e. $C_6H_5 \cdot NH \cdot CO \cdot NH \cdot CO \cdot Et$. [106°]. Formed from phenyl-ethyl-urea and $ClCO_2Et$ (Neubert, B. 19, 1825). Needles (from water).

PHENYL-ETHYL-ALLYL-GUANIDINE $C_{12}H_{17}N_5$ i.e. $CN \cdot H_2 \cdot PhEt \cdot (C_2H_5)_2$. Formed by boiling ethyl-allyl-thio-urea with $NHPh \cdot HgCl$ and alcohol (Forster, A. 175, 41). — B^*HgCl_2 aq.

PHENYL-ETHYL-ALLYL-THIO-UREA $NH(C_2H_5) \cdot CS \cdot NHPh$. [c. 26°]. Formed from allyl-thiocarbimide and ethyl-aniline (Gebhardt, B. 17, 3037). Colourless very soluble crystals.

PHENYL-ETHYL- α -AMIDO-ACETOPHENONE $C_{16}H_{17}NO$ i.e. $C_6H_5 \cdot CO \cdot CH_2 \cdot NPhEt$. [95°]. Formed from α -bromo-acetophenone and diethyl-aniline (Weller, B. 16, 26). Needles.

PHENYL-ETHYLAMIDO-ETHYL SULPHONE $C_8H_9 \cdot SO_2 \cdot C_2H_5 \cdot NHEt$. Formed from $C_6H_5(SO_2C_2H_5)_2$ and ethylamine at 85° (Otto, J. pr. [2] 30, 337). — B^*HCl . [130°]. Needles.

PHENYL-ETHYL-AMIDO-(α)-NAPHTHOQUINONE $C_{16}H_9(NPhEt)O_2$. [155°]. Formed by heating (α)-naphthoquinone (2 pts.) with ethyl-aniline (3 pts.) and $HOAc$ (5 pts.) (Elsbach, B. 15, 1810). Violet needles (from alcohol). — B^*HCl . [c. 230°]. Yellow needles, decomposed by water.

Phenyl-ethyl-amido-(β)-naphthoquinone. [165°]. Formed by heating (β)-naphthoquinone with ethyl-aniline and alcohol (Elsbach, B. 15, 691). Dark-red needles (from ether). Decomposed by boiling $HClAq$ into ethyl-aniline and oxy-naphthoquinone.

PHENYL-ETHYL-AMIDO-PHENOL Ethyl ether $C_{16}H_{15}NO$ i.e. $NPhEt \cdot C_6H_4 \cdot OEt$. (319°). Formed by heating phenyl-*p*-amido-phenol with alcoholic potash and EtI (Phlipa. Calm, B. 17, 2434). Oil.

α -PHENYL-ETHYL-AMINE $C_8H_{11}N$ i.e. $CH_3 \cdot CHPh \cdot NH_2$. (187.5° i.v.). S. 4.166 at 20°. Formed by reducing the phenyl-hydrazide or the oxim of acetophenone in alcoholic solution with $HOAc$ and sodium-amalgam (Tafel, B. 19, 1929; 22, 1856; Kraft, B. 23, 2783). Formed also from acetophenone and sodium formate (Leuckart a. Janssen, B. 22, 1413). Liquid, miscible with alcohol and ether. — B^*HCl . [158°]. — $B^*H_2PtCl_6$. — $B^*H_2SO_4$. [170°]. — $B^*H_2C_2O_4$. [238°]. Prisms, almost insol. alcohol. — $B^*H_2C_2O_4$. Plates, m. sol. boiling alcohol.

Isomerides: — **AMIDO-PHENYL-ETHANE** and **ETHYL-ANILINE**.

Di-phenyl-ethyl-amine $C_{16}H_{19}N$ i.e. $NPh_2 \cdot Et$. Ethyl diphenylamine. (236°) (Girard, Bl. [3] 23, 3); (286°) (Lippmann a. Fleissner, M. 4, 747). Got by heating diphenylamine with alcohol and $HClAq$. Oil.

Di-phenyl-ethyl-amine $CHPh \cdot CH_2 \cdot NH_2$. Formed by reducing di-phenyl-acetonitrile in alcohol with Na (Freund a. Immerwahr, B. 23, 2845). Oil. — B^*HCl . [255°]. V. sol. water.

Di-phenyl-ethyl-amine $CH_3 \cdot Ph \cdot CH_2 \cdot NH_2$. (310°) at 737 mm. Formed by heating deoxybenzoin (1 pt.) with ammonium formate (2 pts.) at 225° (Leuckhart a. Janssen, B. 22, 1409). Liquid, sl. sol. water. Potassium cyanate forms $C_8H_9 \cdot Ph \cdot NH \cdot CO \cdot NH_2$ [99°]. Phenylthiocarbimide forms the corresponding $C_8H_9 \cdot Ph \cdot NH \cdot CS \cdot NHPh$

[170°]; while phenyl cyanate gives the compound $C_6H_5Ph.NH.CO.NHPh$ [129].— $B'HCl$.— $B'HCl$.— $B'HNO_2$; needles.— $B'H_2SO_4$.

Acetyl derivative. [148°]. Needles.

Benzoyl derivative. [178°]. Needles.

Di-phenyl-di-ethyl-amine $NH(CH_2CH_2CH_2Ph)_2$ (336° at 603 mm.). Formed, together with $NH_2CH_2CH_2Ph$ and $N(CH_2CH_2Ph)_3$, by the action of zinc and $HClAq$ on phenyl-acetonitrile (Spica, G. 9, 567). Formed also by distilling $CH_2Ph.CH_2NH_2Cl$ (Fileti a. Piccini, G. 9, 294). Liquid, al. sol. water.— $B'HCl$. [270°]. Pearly scales.— $B'H_2PtCl_6$, m. sol. water.

Tri-phenyl-ethyl-amine $CPh_3.CH_2NH_2$. [116°]. Formed by reducing $CPh_3.CN$ with zinc and $HClAq$ (Elbs, B. 17, 700).— $B'HCl$. [247°].

Tri-phenyl-tri-ethyl-amine $N(CH_2CH_2Ph)_3$. A product of the action of zinc and HCl on phenyl-acetonitrile (Spica, G. 9, 567). Oil.— $B'HCl$. [138°]. Needles, sl. sol. water.

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PHENYL-ETHYL-TRIAZOLE CARBOXYLIC ACID $N.NPh.CE.N \gg C.CO_2H$. [145°]. Got by saponifying its nitrile (Bladin, B. 18, 1548; 25, 177). Melts at 123° when crystallised from water or alcohol, but at 145° when crystallised from benzene.— $B'HCl$: plates.— CuA_2 , 84aq.— AgA_2 : crystalline pp.

Methyl ether MeA' . [41°].

Ethyl ether EtA' . Oil.

Nitrile $C_6H_5N_4$. [38°]. Formed by the action of propionic anhydride on phenyl-hydrazine dicyanide. Converted by alcoholic NH_3 and H_2S into $C_6H_5Ph.Et.CO.NH_2$ [150°] which crystallises in yellow prisms.

Amide $C_6H_5Ph.Et.CO.NH_2$. [152°]. Formed from the nitrile, alcoholic potash, and H_2O . Small prisms, sl. sol. water.

Di-phenyl-di-ethyl-ditriazyl

$C_6H_5N_2$, i.e. $N.NPh \gg C \ll N.NPh$. [187°]. Formed by boiling phenyl-hydrazine dicyanide with propionic anhydride (Bladin, B. 22, 3115). Groups of prisms.— $B'H_2HCl$: minute prisms, decomposed by water.

PHENYL-ETHYL-CARBAMIC CHLORIDE $NPhEt.COCl$. [c. 52°]. Formed from ethyl-amine and CO_2 (Michler, B. 9, 396). Needles.

PHENYL-ETHYL-SEMICARBAZIDE

$C_6H_5N_3O$ i.e. $NHPh.CO.NH.NH.Et$. [112°]. Formed from ethyl-hydrazine and phenyl cyanate (E. Fischer, A. 199, 295). Thin plates, m. sol. hot water. Yields a crystalline nitrosamine.

Phenyl-ethyl-semicarbazide

$NH.Et.CO.NH.NHPh$. [151°]. Formed from phenyl-hydrazine and ethyl cyanate (Fischer, A. 190, 109). Monoclinic tables (from dilute alcohol) $a:b:c = 827:1:1146$; $\beta = 61^\circ$. Gives a bluish-black pp. with cold Fehling's solution, and Cu_2O on warming. Its nitrosamine crystallises from acetone in yellow needles [86.5°].

PHENYL-ETHYL CARBONATE $C_6H_5O_2$ i.e. $C_6H_5O.CO.OEt$. (δ 234°) (P.). S.G. 1.1134 (P.). Formed from $KOPh$ and $CICO_2Et$ (Fatianoff, Z. 1804, 77). Formed also by the action of $AlCl_3$ on a mixture of phenol and $CICO_2Et$ (Pawlewski, B. 17, 1205). Liquid. By long heating at 300° it is split up into Ph_2CO and Et_2CO (Bander, B. 19, 2268).

Reference.—**NITRO-PHENYL-ETHYL CARBONATE. PHENYL-ETHYL-CYANAMIDE**. Formed by boiling phenyl-ethyl-thio-urea in benzene with PbO (Weith, B. 8, 2530). Vitreous mass.

DI-PHENYL-ETHYL-TRICIANIDE

$C_6NPh.Et$. V.D. 129. [57°]. (284° at 15 mm.). Formed by the action of $AlCl_3$ on a mixture of benzonitrile and propionyl chloride at 70° (Krafft a. von Hausen, B. 22, 806).— $B'H_2PtCl_6$.

PHENYL-ETHYLENE v. STYRENE.

s-Di-phenyl-ethylene $C_{12}H_{10}$, i.e. $CHPh.CHPh$. *Stilbene*. Mol. w. 180. [124°]. (307° i.v.). H.C.v. 1,775,600. H.C.p. 1,777,300 (from diamond) (Berthelot a. Vieille, A. Ch. [10] 4, 50); 1,773,331 (Ossipoff, Z. P. C. 2, 646).

Formation.—1. By the dry distillation of benzyl, or benzylidene, sulphide (Laurent, B. J. 25, 616; Maercker, A. 136, 91; Anschütz, A. 235, 206).—2. By distilling benzaldehyde with Na (Williams, Z. 1867, 432).—3. By heating benzoic aldehyde with phenyl-acetic acid and $NaOAc$ at 250°; the yield being 55 p.c. (Michael, Am. J. 313).—4. From *s*-di-phenyl-ethane and Cl (Kade, J. pr. [2] 19, 465).—5. By heating benzylidene chloride with Na or with alcohol and zinc-dust (Limpricht, A. 139, 318; Jippmann, J. 1877, 405).—6. By passing *s*-di-phenyl-ethane through a red-hot tube (Otto a. Droher, A. 154, 177).—7. By heating benzoin with zinc-dust (Limpricht, A. 155, 80).—8. By passing toluene over heated PbO (Behr a. Dörp, B. 6, 754).—9. By heating di-phenyl-acetylene with H and P at 175° (Barbier, J. 1874, 421).—10. By distilling lead phenyl-acetate with sulphur (Radziszewski, B. 6, 390).—11. Together with benzonitrile by the action of zinc-dust and HCl on $C_6H_5.CSNH_2$ (Bamberger, B. 21, 55).—12. By heating di-phenyl-fumarate or di-phenyl-cinnamate (Anschütz, B. 18, 1945).—13. By heating $CHPhBr.CHPhBr$ with alcoholic KSH in a sealed tube at 100° (Auwers, B. 24, 1779).—14. By heating thio-benzoic aldehyde at 190° (Baumann a. Klett, B. 24, 3308).

Properties.—Monoclinic plates, v. sol. ether, sl. sol. cold alcohol. Combines with N_2O , forming $C_{12}H_{10}Ph_2N_2O_2$ [c. 300°] crystallising in needles, sl. sol. hot alcohol (Gabriel, B. 19, 2438). Picryl chloride forms a combination $C_{12}H_{10}C_6H_4(NO_2)_2Cl$ [71°] (Liebermann, B. 8, 378).

Reactions.—1. Yields phenanthrene and toluene when passed through a red-hot tube (Graebe, B. 6, 126).—2. Reduced by $HIAq$ at 150° to *s*-di-phenyl-ethane (Limpricht a. Schwanert, A. 145, 333).—3. Bromine added to an ethereal solution forms a product containing $C_{12}H_{10}Br_2O_2$ [121°] which gives rise to $C_{12}H_{10}Br_2O_2$ [150°] and $C_{12}H_{10}Br_2O_2$ [206°] and when dissolved in alcohol and reduced by sodium-amalgam yields $C_{12}H_{10}O_2$, crystallising from alcohol in flat plates [172°], whence PCl_5 forms $C_{12}H_{10}ClO_2$ [58°], $C_{12}H_{10}Cl_2O_2$ [87°], and $C_{12}H_{10}Cl_3O_2$ [190°] (Limpricht a. Schwanert, A. 153, 121).—4. Fuming HNO_3 added to an ethereal solution forms $C_{12}H_{10}N_2O_2$ [220°], which is converted by boiling alcohol into $C_{12}H_{10}N_2O_2$ [57°-73°] (Lorenz, B. 7, 1097; 8, 1050).

u-Di-phenyl-ethylene CH_2CPh_2 . (277°; [162° at 15 mm.]). Formed by boiling $CHPh_2.CH_2Cl$ with alcoholic potash (Hepp, B. 7, 1409). Formed also by the action of benzene and $AlCl_3$ on

CH_2Br_2 , and on $\text{CHBr}:\text{CBr}_2$ (Demole, B. 12, 2245; Anschütz, A. 235, 154). Liquid. Oxidised by CrO_3 to benzophenone. Combines with Br, forming $\text{CPh}_2\text{Br}:\text{CH}_2\text{Br}$, which readily gives off HBr, and forms bromo-di-phenyl-ethylene [40°] (c. 170° at 11 mm.).

Isomeride. [190°]. A product of the action of alcoholic potash on *exo*-chloro-di-phenyl-ethane (Hepp, B. 7, 1412). Small plates (from ether), v. sl. sol. alcohol.

Tetra-phenyl-ethylene $\text{C}_{20}\text{H}_{20}$, i.e. C_6Ph_4 . Mol. w. 332. [221°]. (193° at 30 mm.).

Formation.—1. By heating CPh_2Cl_2 with finely-divided silver (Behr, B. 3, 751; 5, 277).—2. By heating benzophenone with zinc dust (Staedel, B. 6, 178; A. 194, 367).—3. By strongly heating chloro-di-phenyl-ethane (Engler a. Bethge, A. 174, 194).—4. From CPh_2Br_2 by repeated distillation (Friedel a. Balsohn, Bl. [2] 33, 337).—5. A by-product in the preparation of tri-phenyl-methane from benzene, chloroform, and AlCl_3 (Schwarz, B. 14, 1526).

Preparation.—1. By adding Br to di-phenyl-methane and warming the resulting CHPh_2Br ; the yield is 80 p.c. (Boissieu, Bl. [2] 49, 631).—2. By heating di-phenyl-methane (20 g.) with sulphur (8 g.) for 9 hours to 250°, and finally for one hour to 290°, exhausting with ether, and recrystallising the residue from benzene; the yield is 75 p.c. (Ziegler, B. 21, 780).

Properties.—White needles, v. sol. hot benzene and CS_2 , v. sl. sol. ether. Yields benzophenone (2 mols.) on oxidation (Anschütz, A. 235, 221). Yields a tetrasulphonic acid.

Isomeride C_{10}H_8 , [244°]. Formed by heating (a)-benzopinacol with soda-lime at 370° (Zincke a. Thörner, B. 11, 1397). Needles (from alcohol). Perhaps identical with the preceding.

References.—DI-AMIDO-, BROMO-, DI-CHLORO-, DI-iodo-, NITRO-, NITRO-AMIDO-, and OXY-PHENYLETHYLENE.

PHENYL-ETHYLENE-DIAMINE $\text{C}_{10}\text{H}_{10}\text{N}_2$, i.e. $\text{C}_6\text{H}_5\text{NH}:\text{CH}_2\text{CH}_2\text{NH}_2$. (262° under). Formed by boiling phenyl-amido-ethyl-phthalimide (got from bromo-ethyl-phthalimide and aniline) with conc. HCl (Gabriel, B. 22, 2224). Liquid, miscible with water, forming an alkaline solution. Absorbs CO_2 from the air, forming a crystalline carbonate.— $\text{B}''\text{HCl}$: small greenish needles, acid in reaction.— $\text{B}''\text{HCl}$. Neutral to methyl-orange.— $\text{B}''\text{H}_2\text{Br}_2$.—Picrate [143°]. Flat yellow tables.

Di-acetyl derivative $\text{C}_{10}\text{H}_8\text{Ac}_2\text{N}_2$. [116°]. Crystals, v. c. sol. Aq (Newman, B. 24, 2193).

Di-benzoyl derivative. [143-5°]. Prisms.

Phenyl-di-ethylene-triamine $\text{C}_{10}\text{H}_9\text{N}(\text{C}_6\text{H}_5\text{NH}_2)_2$ (above 300°). Formed by the action of boiling conc. HBr upon its di-phthalyl derivative $\text{NPh}(\text{C}_6\text{H}_4\text{N}:\text{C}_6\text{H}_4\text{O}_2)_2$ [211°], which is a product of the action of aniline on bromo-ethyl-phthalimide at 100°-180° (G.). Thick ammoniacal liquid, miscible with water. Absorbs CO_2 from the air.— $\text{B}''\text{H}_2\text{Br}_2$.—Picrate. [202°]. Needles (from alcohol).

Di-phenyl-ethylene-diamine $\text{C}_{10}\text{H}_{10}\text{N}_2$, i.e. $\text{C}_6\text{H}_5(\text{NHPh})_2$. [63°]. Prepared by heating ethylene bromide (1 mol.) with aniline (4 mols.); the yield being 80 p.c. of the theoretical (Morley, B. 12, 1794; cf. Hofmann, Pr. 10, 104; Grétilat, M. S. [3] 3, 383). Plates, v. sol. alcohol. Yields a di-nitrosamine $\text{C}_6\text{H}_4(\text{NPh.NO})_2$ [187°].

Reacts with benzoic anhydride forming the compound $\text{C}_6\text{H}_5(\text{NPh})_2\text{CHPh}$ [137°], while cuminic, salicylic, anisic, isobutyric, and heptioic aldehydes yield corresponding compounds [125°], [116°], [164°], and [95°] respectively (Moos, B. 20, 732).— $\text{B}''\text{HCl}$.— $\text{B}''\text{H}_2\text{PtCl}_6$.

Mono-acetyl derivative. [128°]. Got by heating the base with chloro-acetic acid and NaOAc at 170° (Bischoff a. Nastvogel, B. 22, 1783).

Di-acetyl derivative. [158°]. Crystals.

Di-phenyl-ethylene-diamine $\text{C}_{10}\text{H}_{10}\text{N}_2$, i.e. $\text{CHPh}(\text{NH})_2\text{CHPh}(\text{NH})_2$. [21°]. Formed, together with benzoic aldehyde, by the action of boiling HCl on $\text{C}_6\text{H}_5\text{N}_2$, which is a product of the action of Na on amarine (Grossmann, B. 22, 2299). Formed also by the action of ammonia on the hydrocyanide of benzoic aldehyde (Lamprecht a. Müller, A. 111, 142). Is perhaps identical with lophine. Plates (from hot water). Reacts with benzoic aldehyde forming $\text{CHPh:N}:\text{CHPh}:\text{CHPh:N}:\text{CHPh}$ [164°], *m*-nitrobenzoic aldehyde forming $\text{C}_6\text{H}_4\text{N}_2\text{O}_2$ [161°], with salicylic aldehyde forming $\text{C}_6\text{H}_3\text{N}_2\text{O}_2$ [205°], and with cuminal forming a compound [168°].— $\text{B}''\text{HCl}$. White needles (from hot water).— $\text{B}''\text{H}_2\text{PtCl}_6$: dark-yellow crystals.

Di-acetyl derivative. [above 350°].

Phthalyl derivative

$\text{C}_{10}\text{H}_8\text{C}_2\text{O}_2\text{N}_2\text{C}_6\text{H}_4\text{Ph}$. [213°]. Minute crystals.

Di-phenyl-di-ethylene-diamine $\text{C}_{10}\text{H}_{10}\text{N}_2$, i.e.

$\text{NPh}(\text{C}_6\text{H}_4\text{NH})_2\text{NPh}$. *Diphenylpiperazine*. *Di-*

phenylpyrazine hexahydride. [163°]. (c. 300°).

Prepared by heating ethylene bromide (1 pt.) with aniline (1 pt.) and NaOAc , and by the action of ethylene bromide on di-phenyl-ethylene-diamine at 120° (Morley, B. 12, 1795; Bischoff, B. 22, 1777; cf. Hofmann, Pr. 9, 277; 10, 104; Lellmann a. Schleich, Pr. 22, 1387; Bischoff, B. 22, 1778). Formed also, by heating pyrazine hexahydride (1 pt.) with bromo-benzene (11 pts.) at 270° (Schmidt a. Wichmann, B. 24, 3233). Needles, sol. alcohol and ether. Its solutions are neutral to litmus. Yields a crystalline di-nitrosoderivative which may be reduced by tin and HCl

to $\text{C}_6\text{H}_5(\text{NH})_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{N}(\text{CH}_2\text{CH}_2)_2\text{NH}_2$ which,

when diazotised and combined with naphthylamine sulphonic acid, yields a colouring matter which dyes cotton.— $\text{B}''\text{HCl}$.— $\text{B}''\text{H}_2\text{PtCl}_6$.

Methyl-iodide $\text{B}''\text{MeI}$. Crystalline. Yields $\text{B}''\text{Me}:\text{PtCl}_6$.

Ethyl-iodide $\text{B}''\text{EtI}$. [100°]. Yields $\text{B}''\text{Et}:\text{PtCl}_6$.

References.—NITRO- and OXY-DI-PHENYL-ETHYLENE-DIAMINE.

• **DIPHENYL-ETHYLENE-DI-BENZYL-DIAMINE** $\text{CHPh}(\text{NHCHPh})_2\text{CHPh}(\text{NHCHPh})_2$. [153°]. Formed by reducing the compound $\text{CHPh}(\text{N}:\text{CHPh})_2\text{CHPh}(\text{N}:\text{CHPh})_2$ [163°], which is itself got by reducing amarine with Na (Grossmann, B. 22, 2301). White needles.

• **DI-PHENYL-ETHYLENE-DICARBAMIC ACID** $\text{C}_6\text{H}_5(\text{NPh.CO}_2\text{H})_2$.

Ethyl ether EtA. [86°]. Needles.

Chloride $\text{C}_6\text{H}_5(\text{NPh.COCl})_2$. [183°]. Formed from di-phenyl-ethylene-diamine and COCl_2 (Hanssen, B. 20, 731). Prisms.

DI-PHENYL-ETHYLENE DI-O-CARBOXYLIC ACID $C_6H_5(CO_2H)_2$. $CH_2=CH.C_6H_4.CO_2H$ [264°]. • Formed by heating for four hours at 215° $CO < \begin{smallmatrix} C_6H_5 \\ O \end{smallmatrix} > CH_2.C_6H_4.CO_2H$ (2 pts.) with K_2CO_3 (5 pts.) (Hasselbach, A. 243, 258). Small needles (from dilute HOAc). Changes on heating into the parent acid [196°]. Reduced by conc. HIAq to $C_6H_5(C_6H_4.CO_2H)_2$ [185°].— Ag_2A'' . Flocculent pp.

Ethyl ether Et.A''. [80°]. Needles.

Isomeride v. DI-PHENYL-MALEIC ACID.

References.—NITRO- and OXY- DI-PHENYL-ETHYLENE CARBOXYLIC ACIDS.

DI-PHENYL-ETHYLENE-DI-ETHYL-DIAMINE $C_{12}H_{18}N_2$ i.e. $C_6H_5(NPhEt)_2$. [70°]. Formed from di-phenyl-ethylene-diamine and EtH (Hofmann, Pr. 10, 104).— $B''HCl$.— $B''H_2PtCl_6$: needles.

PHENYL-ETHYLENE-GLYCOL v. DI-ETHYL-ETHYL-BENZENE.

DI-PHENYL-ETHYLENE-DI-HYDRAZINE $C_{12}H_{18}N_4$ i.e. $C_6H_5(NPh.NH_2)_2$. [90°]. Formed from sodium phenyl-hydrazine and ethylene bromide in benzene (Burchard a. Michaelis, B. 21, 3202; A. 254, 116). Prisms or plates. Aldehyde forms $C_6H_5(NPh.N:CHMe)_2$. [82°]. Benzoin aldehyde forms an analogous body [193°]. Acetone and acetophenone form analogous compounds [72°] and [118°]. Phenyl-thiocarbinate forms $NH_2.NPh.C_6H_5.NPh.NH.CS.NHPh$ [161°] and $C_6H_5(NPh.NH.CS.NHPh)_2$ [194°]. Yields a crystalline nitroso-derivative [160°]. $SOCl_2$ forms $C_6H_5(NPh.N:SO)_2$. [123°] (Michaelis a. Ruhl, A. 170, 123).— $B''HCl$. [212°]. Needles, st. sol. HClAq. — $B''H_2SO_4$. — $B''H_2NO_3$. [173°]. — $B''H_2C_2O_4$. [183°].

Acetyl derivative $C_{12}H_{18}Ac_2N_4$. [223°].

Succinyl derivative $C_{12}H_{18}N_4.C_4H_4O_4$. [c. 126°].

Succinozyl derivative.

$C_{12}H_{18}(NPh.NH.CO.C_6H_5.CO_2H)_2$. [203°].

Oxalyl derivative $C_{12}H_{18}N_4.C_2O_4$. [c. 183°].

• **Di-phenyl-di-ethylene-dihydrazine** $(C_6H_5)_2(N.HPh)_2$. [178°]. Got by heating phenyl-hydrazine with $C_6H_5Br_2$ and alcohol (Markwald, C. C. 1888, 1410).

DI-PHENYL-ETHYLENE DIKETONE

$C_6H_5.CO.CH_2.CH_2.CO.C_6H_5$. *Diphenacyl Succinophenone*. [134°] (A.); [140°] (C.); [142°-145°] (P.). *Formation.*—1. Together with the isomeric $CH_2.CO$ $CH_2.CPh_2 > O$, by the action of succinyl chloride and $AlCl_3$ on benzene (Anger, A. Ch. [6] 22, 312; Claus, B. 20, 1374).—2. From acetophenone by treatment with fuming HNO_3 and reduction of the resulting $C_6H_5.H_2N.O$, by zinc-dust and HOAc (Tollmann, B. 20, 3361).—3. By the action of KOHAq on di-benzoyl-propionyl acid suspended in alcohol (Paal, B. 21, 3056).

Properties.—Needles, v. sol. ether.

Oxim $C_6H_5(CPh:NOH)_2$. [204°].

Phenyl-hydrazide $C_6H_5(CPh:N.HPh)_2$. [180°]. Needles, v. sol. ether.

DI-PHENYL-ETHYLENE DIKETONE CARBOXYLIC ACID v. PHENACYL-BENZOYL-ACETIC ETHER.

Di-phenyl-ethylene diketone di-o-carboxylic acid $C_6H_5O_2$ i.e. $C_6H_5(CO.O_2H)_2$. [172°]. Obtained by boiling di-phthalyl-ethane with

alkalis (Gabriel a. Michael, B. 10, 1561, 2199; Roser, B. 17, 2622; 18, 803, 8115; Baumann, B. 20, 1486). Prisms (from water), v. sol. alcohol. Reconverted by conc. H_2SO_4 into di-phthalyl ethane $C_6H_5(C_6H_4.CO_2H)_2$. A boiling alcoholic solution of phenyl-hydrazine forms $C_6H_5.H_2N.O_2$ [237°]. Hydroxylamine at 100° gives rise to $C_6H_5(C < \begin{smallmatrix} C_6H_5 \\ N.O \end{smallmatrix} > CO)_2$. [270°] (Baumann, B. 20, 1492).— Ag_2A'' : small plates, sl. sol. hot water.

(a) *Anhydride* $C_{12}H_{10}O_2$. [230°]. Got by heating the acid alone, or together with diphthalyl-ethane, by heating it for a short time with HCl. Needles (from alcohol).

(b) *Anhydride* $C_{12}H_{10}O_2$. [202°]. Formed by more prolonged heating of the acid with HCl, and also, together with the (a)-isomeride, by heating the acid by itself. Prisms (from alcohol). Both anhydrides are reconverted into the acid by boiling alkalis, and into di-phthalyl-ethane by elimination of H_2O .

Isomeride v. DI-BENZOYL-SUCCINIC ACID.

PHENYL-ETHYLENE OXIDE $\begin{smallmatrix} CH_2 \\ CHPh > O \end{smallmatrix}$.

[260° at 50 mm.]. Formed by heating di-oxethyl-benzene with dilute H_2SO_4 (Breuer a. Zincke, B. 11, 1402). Oil. Converted by PBr_3 into $CHPh.Br.CH.Br$.

Tetra-phenyl-ethylene oxide v. BENZOPINACOLIN.

PHENYL-ETHYLENE SULPHIDE

$CH_2 > S$. S.G. 1.099. Formed from $CHPh.Br.CH_2.Br$ by successive treatment with alcoholic KSHaq (Spring a. Marsenille, B. [3] 7, 13). Oil with strong smell, sol. alcohol-ether. Oxidised by CrO_3 to benzoic acid.

Di-phenyl-ethylene sulphide $\begin{smallmatrix} CHPh \\ CHPh > S \end{smallmatrix}$.

[169°]. A product of the distillation of benzyl sulphide (Barbier, J. 1876, 421). Needles.

Di-phenyl-ethylene disulphide $C_6H_5(SPh)_2$. [65°]. Formed from NaSPH and $C_6H_5Br_2$ (Ewerlöf, B. 4, 716). Needles, insol. water.

DI-PHENYL-ETHYLENE DISULPHONE

$C_6H_5(SO_2C_6H_5)_2$. [180°].

Formation.—1. By oxidation of $C_6H_5(SPh)_2$ (Ewerlöf, B. 4, 717).—2. By boiling sodium benzene sulphinat (100 pts.) with $C_6H_5Br_2$ (58 pts.) in alcohol (Otto, B. 13, 1279; J. pr. [2] 30, 174). 3. By adding $CH_2.CCl_2.CO_2Na$ (1 mol.) to $C_6H_5.SO_2Na$ (2 mols.) in weak alcoholic solution, kept neutral by Na.CO₃ (Otto, J. pr. [2] 40, 531). 4. By heating $CH_2.CCl_2$ with $C_6H_5.SO_2Na$ at 160° (Otto, B. 21, 1651).

Properties.—Triclinic needles or plates, sl. sol. water, m. sol. alcohol, v. sol. HOAc.

Reactions.—1. *Sodium amalgam* reduces it to alcohol and $C_6H_5.SO_2Na$, which is finally reduced to $C_6H_5.SNa$.—2. *Chlorine* in diffused daylight forms $C_6H_5Cl_2$ and benzene sulphonio chloride. In sunlight the products are $C_6H_5Cl_2$, SO_2Cl_2 , and chlorinated benzenes.—3. Boiling aqueous KOH splits it up into $C_6H_5.SO_3K$ and $C_6H_5.SO_3C_6H_5.OH$. Conc. KOHAq forms a compound [88°] crystallising from alcohol.—4. Aqueous NH_3 forms $C_6H_5.SO_2ONH_2$ and $(C_6H_5.SO_2CH_2.CH_2)_2NH$ [78°] which yields $BHCl$ [193°], $B''H_2PtCl_6$, a nitrate [190°], and the derivatives $(C_6H_5.SO_2CH_2.CH_2)_2NMe$ and $(C_6H_5.SO_2CH_2.CH_2)_2NMe.HCl$ [221°].—5. Aqueous

ethylamine forms $C_6H_5SO_2NH_2Et$ and $C_6H_5SO_2C_2H_5NH_2Et$, an oil which yields $BHCl$ [180°].—6. Alcoholic KCy forms $C_6H_5SO_2K$ and $C_6H_5(CN)$.

PHENYL-ETHYLENE-THIO-UREA

$CS \begin{smallmatrix} NPh \\ NH \end{smallmatrix} > C_6H_5$. [155°]. Formed from phenyl-ethylene-diamine and CS_2 (Newman, B. 24, 2191). White plates, v. sol. alcohol.

Di-phenyl-ethylene- θ -thio-urea

$C_6H_5 \begin{smallmatrix} NPh \\ S \end{smallmatrix} > C_6H_5$. [136°]. (above 300°). Formed by heating di-phenyl-thio-urea with ethylene bromide (Will, B. 14, 1490; 15, 343). Plates (from alcohol), $KClO_3$ and HCl form $C_6H_5N_2SO_2$ [187°] (Andreasch, M. 4, 134).— $B^*H_2SO_4$; thick prisms, v. sol. water.

Di-phenyl-ethylene- θ -thio-di-urea

$C_6H_5N_2S_2$ i.e. $C_6H_5(NHCS.NHPh)_2$. [193°]. Formed from $C_6H_5(NH_2)_2$ and phenyl-thio-carbimide in alcohol (Lellmann a. Würstner, A. 228, 234). White scales, insol. alcohol, sl. sol. $HOAc$. Decomposed by heat, giving di-phenyl-thio-urea and a crystalline body [164°].

PHENYL-ETHYLENE-UREA

$C_6H_5 \begin{smallmatrix} NPh \\ NH \end{smallmatrix} > CO$. [161°]. Formed from phenyl-ethylene-diamine hydrochloride and potassium cyanate, NH_3 being given off (Newman, B. 24, 2192). Plates, v. sol. alcohol, insol. cold water.

Di-phenyl-ethylene-urea

$CH_2.NPh \begin{smallmatrix} CH_2.NPh \\ NH \end{smallmatrix} > CO$. [209°]. Formed by the action of $COCl_2$ in benzene on $C_6H_5(NHPh)_2$; an intermediate body being $C_6H_5N_2Cl_2O$ (Michler a. Keller, B. 14, 2183; Hanssen, B. 20, 784). Plates.

PHENYLETHYL-ETHYL-PYRIDINE

$C_{10}H_{11}N$ i.e. $N \begin{smallmatrix} C(CH_2CH_2Ph) \\ CH_2CH_2 \end{smallmatrix} CH_3$ (316° cor.). S.G. 1.016. Formed by reducing styryl-ethyl-pyridine with $HIAq$ at 165° (Plath, B. 21, 3693; 22, 1057). Oil, v. sl. sol. water, v. sol. alcohol and ether, volatile with steam. Yields $C_{10}H_{11}Br.N$ [128°] whence $AgOAc$ forms $C_{10}H_{11}(OAc).N$ (815°-320°).— $B^*H_2PtCl_6$. [168°]. Yellow needles.— B^*HHgCl_2 . [136°]. Needles.— B^*HAuCl , aq: crystalline mass.

Hexahydride $C_{10}H_{11}N$. (314°). S.G. 1.9668. Got by reducing the preceding body in alcohol with Na . Oil, sl. sol. water, miscible with alcohol and ether.

PHENYL-ETHYL-PURFURANE

$C_6H_5CH_2CH_2C_2H_5O$. (241°). A product of the action of Na on an alcoholic solution of $C_6H_5OCH_2C_6H_5$, which is formed by condensation of furaldehyde with phenyl-acetonitrile (Freund a. Immerwahr, B. 23, 2848). Oil, smelling like CH_3Ph .

DI-PHENYL-ETHYL-GUANIDINE

$C_{10}H_{11}N_3$ i.e. $NH_2Et.C(NPh).NHPh$. Got from phenyl-ethyl-cyanamide and aniline at 100° (Weith, B. 8, 1531). Crystalline.— $B^*H_2PtCl_6$.

* **PHENYL-ETHYL-HYDANTOIN** $C_{10}H_{11}N_3O_2$ i.e. $CHPh \begin{smallmatrix} CO.NEt \\ NH.CO \end{smallmatrix}$ [94°]. Formed from phenyl-hydantoin, alcoholic KOH , and EtI (Pinner, B. 21, 2325). Prisms, v. sol. alcohol, sl. sol. cold water. Decomposed by baryta into ethylamine and phenyl-amido-acetic acid.

Phenyl-ethyl- ψ -hydantoin

$CHPh \begin{smallmatrix} CO.NEt \\ O-C.NH \end{smallmatrix}$ Separates from a dilute alkaline solution of the preceding isomeride on standing. Slender needles, insol. water, nearly insol. alcohol. Decomposed by heating with baryta-water into NH_3 , NH_4Et , and α -oxy-phenyl-acetic acid.

* **PHENYL-ETHYL-HYDRAZINE** $C_6H_5N_2$ i.e. $NPhEt.NH_2$. (230°). Formed by reducing the p-trosamine of ethyl-aniline with zinc-dust, $HOAc$, and alcohol (Fischer, B. 8, 1642; A. 199, 325; Phillips, B. 26, 2485). Formed also from $EtBr$ and $NPhN_2NH_2$ in benzene (Michaelis a. Phillips, A. 252, 270). Oil. Reduces Fehling's solution on warming. Oxidised by HgO to diphenyl-di-ethyl-tetrazone $NPhEt.N:N.NPhEt$ [108°]. $SOCl_2$ forms oily $NPhEt.NSO$ (Michaelis, B. 22, 2234).— B^*HCl . Plates.

* *Acetyl derivative* $NEtPh.NHAc$. [80°]. *Ethyl-bromide* $NH_2.NPhEt.Br$. Tri-metric prisms (from alcohol); $d_{40} = 822.1$; $n_D^{20} = 1.527$.

V. e. sol. water, insol. ether. Decomposes at 193°. Insol. $KOHAq$. Converted by moist Ag_2O into a caustic hydroxide. Yields also $(NH_2.NPhEt)_2H_2Fe.Cy_2$ (Fischer, A. 190, 187).

Ethyl-chloride $NH_2.NPhEt.Cl$. [198°]. Needles, v. e. sol. water. $B^*Et.PtCl_6$.

* *Ethyl-iodide* $NH_2.NPhEt.I$. [145°].

s-Phenyl-ethyl-hydrazine

$NHPh.NH_2Et$. Formed, together with the preceding isomeride, by heating phenyl-hydrazine with $EtBr$. The crude product is dissolved in water mixed with $NaOHAq$, and the ptd. oil extracted with ether. The ethereal solution is freed from phenyl-hydrazine by HCl and the filtrate oxidised by HgO . On addition of HCl it deposits di-phenyl-di-ethyl-tetrazone, and the mother-liquor yields by steam-distillation oily $C_6H_5N_2.NEt$ [175°-185°]. The $NH_2.NEt$ is then reduced by sodium-amalgam (Ehrhardt a. Fischer, B. 11, 613).

Properties.—Oil, sol. alcohol and ether. Readily reduces Fehling's solution and HgO . Zinc-dust and $HOAc$ yield aniline and ethylamine.— $B^*H_2C_2O_4$; needles, v. sol. hot water.

DI-PHENYL-ETHYLIDENE-DIAMINE v. Ethylidene-di-aniline, vol. ii. p. 496.

DI-PHENYL-ETHYLIDENE-DI-ETHYL-DIAMINE $C_{14}H_{17}N_2$ i.e. $CHMe(NPhEt)_2$. Formed from ethyl-aniline and aldehyde (Schiff, A. 140, 95; cf. Schultz, B. 16, 2601). Thick liquid.— $B^*H_2PtCl_6$.

PHENYL-ETHYLIDENE-DI-ETHYL-DI-SULPHONE $CH_2.CPh(SO_2Et)_2$. [101°]. Formed from benzylidene di-ethyl di-sulphone, MeI , and $EtONa$ (Fromm, A. 253, 154). Needles.

PHENYL-ETHYLIDENE-HYDRAZINE $CH_2.CPh:N.NH_2$. (255°). Formed from acetophenone and hydrazine hydrate (Curtius, J. pr. [2] 44, 540). Liquid. Yields $CH_2.CPh:N:N.CHPh$ [59°] and $N(CPh.CH_2)_2$ [121°].

DI-PHENYL-ETHYLIDENE-DISULPHONE $CH_2.CPh(SO_2Ph)_2$. [102°]. Got by oxidising $CH_2.CPh(SPh)_2$ or $CH_2.C(SPh)_2.CO_2H$ with dilute (1 p.c.) $KMnO_4$ (Escalas a. Baumann, B. 19, 2815). Needles or thin lamellae, insol. water, acids, and alkalis, sl. sol. alcohol and ether. Not attacked by alcoholic potash at 140°.

PHENYL-ETHYLIDENE-DI-THIO-DI-GLYCOLLIC ACID $CH_2.CPh(SCH_2.CO_2H)_2$.

Billeter a. Strohl, *B.* 21, 108). Yellow needles, sol. alcohol.

PHENYL-ETHYL-THIOCARBAMIC ACID NPhEt.CS.OH.

Ethyl ether EtA. [187]. (143° at 12 mm.). S.G. 1.066. Formed from NPhEt.CS.Cl and NaOEt (Billeter a. Strohl, *B.* 20, 1629; 21, 04). Crystals.

Phenyl ether PhA. [69]. Formed from he chloride and phenol. Flat needles.

Chloride NPhEt.CS.Cl. [57]. Formed from ethyl-aniline and CS₂. Prisms (from grain). Converted by alcohol into (NPhEt.CS.)O [143°], S. (alcohol) 7 at 15°.

Phenylethyl-thiocarbamic acid. Phenyl-thylamine salt

H₂Ph.NH.CS.NH₂.C₂H₅Ph [130°]. Formed from phenylethylamine and CS₂ (Neubert, *B.* 19, 825). Sol. hot water and alcohol.

Phenyl-ethyl-di-thio-carbamic acid NPhEt.CS.SH.

Ethyl ether EtA. [67]. (305° 315). Formed by heating NPh.C(NPhEt).SEt with S₂ at 160° (Bernthsen a. Fricke, *B.* 15, 568, 533). Formed also from NPhEt.CS.Cl and NaSEt (B. a. S.). Prisms (from ether). Forms a crystalline compound with MeI.

Phenyl ether PhA. [127]. Formed from NPhEt.CS.Cl and PhSH (B. a. S.). Needles.

PHENYL-ETHYL-THIO-SEMI-CARBAZIDE NH₂Et.CS.NH.NHPh. [122]. Formed from ethyl-thiocarbamide and phenyl-hydrazine (Dixon, *J.* 55, 302). White crystals, v. sl. sol. water. FeCl₃ gives a red colour changing to blackish-green.

Isomeride NHPh.CS.NH.NH₂Et. [110°]. Formed from phenyl-thiocarbamide and ethyl-hydrazine (Fischer, *A.* 199, 296). Needles.

Di-phenyl-ethyl-thio-semi-carbazide NPhEt.CS.NH.C₂H₅Ph. [149]. Formed from α-phenyl-ethyl-hydrazine and phenyl-thiocarbamide (Michaëlis a. Phillips, *A.* 252, 273).

PHENYLETHYL-THIO-ARIMIDE C₂H₅Ph.NCS. Formed from phenylethyl-amine by successive treatment with CS₂ and HgCl₂ (Neubert, *B.* 19, 1825). Yellow oil.

PHENYL ETHYL DITHIOCARBONATE CS(OEt)(SPh). Formed by mixing solutions of C₂H₅N₂Cl and potassium ethyl dithiocarbonate at 0° (Leuckart, *J. pr.* [2] 41, 186). Reddish-yellow oil, sl. sol. water, slightly volatile with steam. Converted by heating with alcoholic NH₃ into phenyl mercaptan and ammonium sulphocyanide.

PHENYLETHYL-THIOHYDANTOIN

C₂H₅N₂SO i.e. C₂H₅Ph.N:C<S-CH₂ or CS<N(C₂H₅)CH₂. The hydrochloride E.HCl [138°] is formed from phenylethyl-thio-urea and chloro-acetic acid (Neubert, *B.* 19, 1822).

PHENYL-ETHYL-THIOPHENE C₂H₅Ph.S i.e. S<CPh:CH. [40°]. Obtained by heating CH₂Bz.CH₂Et.CO₂Na with P₂S₅ (Dittrich a. Paul, *B.* 21, 3457). Small plates. Gives a cherry-red colour with Hatin and H₂SO₄ and a bluish-green colour with phenanthraquinone and HOAc.

PHENYL-ETHYL-THIO-UREA C₂H₅Ph.NS i.e. NPhEt.CS.NH₂. [126°]. Formed from ethyl-

aniline hydrochloride and potassium sulphocyanide (Gebhardt, *B.* 17, 2094). Large pearly prisms (from alcohol).

Benzoyl derivative NPhEt.CS.NH₂Bz. [134°]. Formed from ethylaniline and benzoyl-thiocarbamide (Dixon, *C. J.* 55, 305). Pale lemon-yellow prisms, insol. water, sol. alcohol.

s-Phenyl-ethyl-thio-urea NHPh.CS.NH₂Et. [99°]. Formed from phenyl-thiocarbamide and NH₂Et and from ethyl-thiocarbamide and aniline (Weith, *B.* 8, 1524; Michael a. Palmer, *Am. C.* 260). Monoclinic crystals.

Phenylethyl-thio-urea NH₂.CS.NH.C₂H₅Ph. [123°]. Formed from phenylethyl-amine hydrochloride and potassium sulphocyanide (Neubert, *B.* 19, 1822). Plates (from dilute alcohol).

Phenyl-ethyl-ψ-thio-urea NHPh.C(SEt):NH. Formed from phenyl-thio-urea and EtI (Bertram, *B.* 25, 55). Yields mercaptan on treatment with alkalis. B.HI. [103°]. - B₂H₄N₂O₇. [196°].

Phenyl-di-ethyl-ψ-thio-urea NPhEt.C(SEt):NH. Formed from the preceding body and EtI (B.). B.HI. - B₂H₄N₂O₇. [148°]. - B₂H₄N₂O₇. [170°].

Phenyl-tri-ethyl-ψ-thio-urea NPhEt.C(SEt):NEt. [c. 275°]. Got from the preceding and EtI (B.). - B₂H₄N₂O₇. [c. 96°]. - B₂H₄N₂O₇. [135°].

Di-phenyl-ethyl-thio-urea NHPh.CS.NHPh. [89°]. Formed from phenyl-thiocarbamide and ethyl-aniline (Gebhardt, *B.* 17, 2090). Crystals.

Di-phenyl-ethyl-ψ-thio-urea NHPh.C(SEt):NPh. [79°]. Formed from di-phenyl-thio-urea and EtI (Rathke, *B.* 14, 1776) and by the action of mercaptan on C(NPh), in the cold (Will, *B.* 15, 1308). Needles (from dilute alcohol). Decomposed by heat into C(NPh), and EtSH. Cl passed into a solution of its hydrochloride yields ethane sulphonic acid. B.HCl. - B₂H₄N₂O₇. 2aq. - B.HI aq. [157-5°] (Bernthsen, *B.* 15, 266, 567).

Di-phenyl-di-ethyl-thio-urea CS(NEtPh)₂. [75-5°]. Formed from NPhEt.CS.Cl and ethyl-aniline at 100° (Billeter, *B.* 20, 1631). White tables (from ligroin) or needles (from alcohol).

Di-phenyl-di-ethyl-ψ-thio-urea CS(NH.C₂H₅Ph)₂. [84°]. Formed from phenyl-ethyl-amine and alcoholic CS₂ (Neubert, *B.* 19, 1824). Plates (from alcohol), insol. water.

Acetyl derivative C₂H₅Ph.N₂SO. [73°].

Di-phenyl-di-ethyl-ψ-thio-urea NPhEt.C(SEt):NPh. Oil. The hydro-iodide, got by heating di-phenyl-ethyl-ψ-thio-urea with EtI at 130°, is crystalline (B. a. F.).

α-PHENYL-ETHYL-UREA NPhEt.CO.NH₂. [62°]. Formed from ethyl-aniline hydrochloride and potassium cyanate (Gebhardt, *B.* 17, 2095).

s-Phenyl-ethyl-urea NHPh.CO.NH₂Et. [99°]. Formed from ethyl cyanate and aniline (Wurtz, *C. R.* 32, 417). Needles (from dilute alcohol). Yields a nitro-amine NHPh.CO.NE₂NO [60°] crystallising in monoclinic prisms (E. Fischer, *A.* 199, 286).

Phenylethyl - urea NH₂.CO.NH.C₂H₅Ph. [112°]. Formed from β-phenyl-ethyl-amine and potassium cyanate (Spica, *G.* 9, 568). Flat prisms, m. sol. cold water.

Phenyl - di - ethyl - urea NHPh.CO.NE₂. [85°]. Formed from phenyl cyanate and NH₂Et (Gebhardt, *B.* 17, 3039). Needles.

furfuraldehyde in alcohol (Goldschmidt a. Poltzer, *B.* 24, 1007). Needles. — $B'HCl$: plates. — $B'H_2PtCl_6$. Light-yellow crystalline pp.

(8) **PHENYL-(7)-FURFURYL-PROPYLAMINE** $C_6H_5O_2CH_2CHPh.CH_2NH_2$. (283°). Formed from phenylacetone and furfuraldehyde, the product of condensation of these bodies $C_6H_5O_2CH_2CHPh.CN$ being reduced by Na and dry alcohol (Freund a. Immerwahr, *B.* 23, 2850). Oil, with alkaline reaction. Converted by nitrous acid into the liquid alcohol $C_6H_5O_2CH_2CHPh.CH_2OH$. Phenyl thiocarbamide forms $C_6H_5O_2C_6H_4Ph.NH.CS.NHPh$ [113]. — $B'HCl$. [176°]. Crystalline, v. sol. water. Reacts with potassium cyanate forming $C_6H_5O_2C_6H_4Ph.NH.CO.NH_2$ [101°]. — Mercury double salt: [175°]; needles. — Picrate: [152°]. Yellow crystalline powder.

PHENYL-FURIDANE Dihydrate

$CPh \begin{smallmatrix} CH_2CH \\ O-CH_2 \end{smallmatrix} CH_2$. • (250° at 721 mm.). Formed by heating its carboxylic acid at 200° (Perkin, *C. J.* 51, 731). Oil. HBr forms $C_6H_5.CO.C_6H_4Br$.

PHENYL-FURIDANE DIHYDRIDE CARB.

• **OXYLIC ACID** $CO_2H.C \begin{smallmatrix} CH_2CH \\ CPh.O \end{smallmatrix} CH_2$.

Phenylidichloroacetone carboxylic acid. [c. 144°]. Formed by saponifying its ether, which is not by the action of $NaOH$ on a mixture of trimethylene bromide and benzoyl-acetic ether (Perkin, *C. J.* 51, 726). Monoclinic prisms (from ether); $abce = 2.638:1.3398$; $\beta = 74^\circ 44'$. — AgA' : needles (from water).

Ethyl ether EtA'. [60°]. Prisms.

PHENYL-GLUTARIC ACID $C_6H_4O_2$, i.e. $CHPh(CH_2CO_2H)_2$. [138°]. Formed by heating sodium malonic ether with alcohol and cinnamic ether at 100°, saponifying the resulting ether $CH(CO_2Et)_2CHPh.CH_2CO_2Et$, and heating the acid at 110° (Michael, *J. pr.* [2] 35, 352; *Ann.* 9, 110). Needles, sl. sol. water, m. sol. alcohol. — AgA' : amorphous pp.

Di-phenyl-glutaric acid $CH_2(CHPh.CO_2H)_2$. [164°]. Formed by saponifying its nitrile (Zelinsky a. Feldmann, *B.* 22, 3232). Needles.

Nitrile $CH_2(CHPh.CN)_2$. [71°]. Formed by heating $CHPh.CN$ with CHI_3 and dry $NaOH$.

PHENYL-GLYCERIC ACID v. **O-oxo-phenyl-propionic acid**.

TRI-PHENYL GLYCERYL TRIKETONE $CH.Bz.CH(Bz).CH(Bz)$. *Tri-benzoyl-propane*. [137°]. Formed from tricarballic chloride, benzene, and $AlCl_3$ (Emery, *B.* 21, 601). Straw-yellow needles. Yields a phenyl-hydrazide [57°-60°].

PHENYL-GLYCIDIC ACID $C_6H_5O_2$, i.e. $O \begin{smallmatrix} CHPh \\ CH.CO_2H \end{smallmatrix}$ *Phenyl-pyruvic acid?* [155°]

Formed by boiling benzoyl-imido-phenyl-propionic acid $NBz \begin{smallmatrix} CHPh \\ CH.CO_2H \end{smallmatrix}$ with aqueous HCl or with KOH (Plöchl, *L.* 16, 2817; 19, 3167). Formed also by boiling phenyl-oxalacetic acid with dilute H_2SO_4 (W. Wislicenus, *B.* 20, 592). Plates, v. e. sol. alcohol and ether. $FeCl_3$ colours its alcoholic solution green. Sodium-amalgam reduces it to α -oxy-phenyl-propionic acid. Yields an oxim and a phenyl-hydrazide $CHPh.CN.HPh.CO_2H$ [161°]. Toluene-o-diamine forms a quinoxaline (Erlenmeyer, jun.,

B. 19, 2570; 20, 2465; 22, 1482). Aniline forms $C_6H_5Ph(NHPh)(OH).CO_2H$.

(8) **Phenyl-glycidic acid**. Formed from $C_6H_5.CH(OH).CHCl.CO_2H$ and cold alcoholic potash (Glaser, *A.* 147, 98). Oil, crystallising at 0°. Decomposes, even at 15°, into phenyl-acetic aldehyde and CO_2 . Boiling dilute H_2SO_4 forms $CHPh(OH).CH(OH).CO_2H$ and phenyl-acetic aldehyde (Erlenmeyer a. Lipp, *A.* 219, 181). Yields β -oxy-phenyl-propionic acid on reduction with sodium-amalgam. — NaA' . — KA' . — AgA' : crystalline powder.

Ethyl ether EtA'. (280° cor.). Oil.

References.—NITRO- and OXY-PHENYL-GLYCIDIC ACID.

PHENYL-GLYCOCOLL v. **PHENYL-AMIDO-ACETIC ACID**.

PHENYL-GLYCOL v. **DI-OXY-ET- α -BENZENE**.

PHENYL-GLYCOLLIC ACID v. *Phenyl-derivative of GLYCOLLIC ACID and MANDELIC ACID*.

Di-phenyl-glycollic acid v. **BENZILIC ACID**.

PHENYL-GLYCOLLIC ACRYLIC ACID v.

Carboxymethyl derivative of COMMANIC ACID.

• **PHENYLGLYCOLYL-TROPEINE** $C_{12}H_{19}NO_3$.

Homo-atropine. [98°]. Formed by heating tropine mandelate with $HClAq$ (Ladenburg, *A.* 217, 82). Deliquescent prisms (from ether), m. sol. water. Less poisonous than atropine. — $B'HAuCl_4$. — $B'HIb$. — $B'C_6H_5N_3O_3$. Yellow plates.

TETRA-PHENYL-GLYCOSINE v. **GLYCOSINE**.

PHENYL-GLYOXAL $C_6H_5.CO.CHO$. (142° at 125 mm.). Formed by allowing a mixture of its mono-oxim (30 g.) with $NaHSO_4$ (120 g. of a 35 p.c. solution) to stand till all is dissolved, and then adding H_2SO_4 and distilling (Müller a. von Pechmann, *B.* 20, 2904; 22, 2557). Oil. Forms a crystalline hydrate [73°]. Converted by HNO_3 into phenyl-glyoxylic acid, and by potash into mandelic acid. Ammonia forms $C_{12}H_{19}N_3O_3$ or $C_{12}H_{17}N_3O_3$ crystallising in plates [193°] which can be distilled. Hydroxylamine gives $C_6H_5H_2N_2O_3$, [219°], sol. alkalies.

Mono-oxim $C_6H_5.CO.CH.NOH$. *Nitroso-acetophenone*. [128°]. Formed from acetophenone, isocyanil nitrite, and alcoholic $NaOEt$ (Claisen, *B.* 20, 656, 2194; Braun, *B.* 22, 556). Monoclinic tables (from chloroform), sl. sol. cold water, v. sol. alkalies. Yields $C_6H_5.CO.CN$ on warming with Ac_2O . Boiling $NaOHaq$ forms $NaCy$ and $NaOBz$. Its acetyl derivative is converted by $NaOHaq$ into $CHBz(OH).CO.CO.C_6H_5$, [170°] crystallising in minute needles (Söderbaum, *B.* 24, 1386, 3031).

Di-oxim $C_6H_5C(NOH).CH(NOH)$. *Anti-phenyl-amphi-glyoxim*. [162°] (S.); [168°] (R.). Formed by the action of hydroxylamine on the mono-oxim, or on mono- or di-bromo-acetophenone (Schramm, *B.* 16, 2183; Strassmann, *B.* 22, 3419; Russanoff, *B.* 24, 3501). Small needles, v. sol. alcohol, insol. $CHCl_3$; subliming below 160°. N_2O_4 gives $C_6H_5C_2HN_2O_4$ [c. 90°] crystallising in colourless prisms (Schöll, *B.* 23, 3504). By dissolving in ether and treating with HCl it is converted into an isomeride [180°]. This body, called phenyl-anti-glyoxim, is v. sol. Ac_2O and yields a di-acetyl derivative [92°]. Phenyl-anti-glyoxim is only stable in acid solutions being readily re-converted into the original di-oxim [168°]. By treatment of the di-oxim [168°] $NaOHaq$ and CO_2 at -10° there is formed a

(Fischer, *B.* 17, 578; Ebers, *A.* 227, 340). May be reduced to $C_6H_5.OH(N_2H_5Ph).CO.H$ [158°], and finally to aniline and α -amido-phenyl-acetic acid.

Phenyl-methyl-hydrazide
 $C_6H_5.C(N_2MePh).CO_2H$ [116°]. Plates (from alcohol). Its amide $C_6H_5.C(N_2MePh).CONH_2$ [156°] is crystalline.

Phenyl-ethyl-hydrazide
 $C_6H_5.C(N_2EtPh).CO_2H$ [109°]. Formed, together with its amide $C_6H_5.C(N_2EtPh).CO.NH_2$ [111°], by the action of phenyl-ethyl-hydrazine in dilute HOAc on phenyl-glyoxylic acid. Yellow plates, sl. sol. water. Yields ethyl-aniline and benzoic aldehyde when heated with conc. HClAq.

References.—AMIDO-, NITRO-, and OXY-PHENYL-GLYOXYLIC ACID.

PHENYL-GLYOXYLIC^o - CARBOXYLIC ACID $C_6H_5.(CO_2H).CO.CO_2H$ [140°]. Formed by oxidising the oxynone $C_{10}H_8O_3$ or indonaphthene dihydride carboxylic acid with alkaline $KMnO_4$ (Scherks, *B.* 18, 378; cf. Zincke, *A.* 226, 53; 240, 142). Yields CO_2 and phthalic anhydride on heating. May be reduced to phthalic carboxylic acid.— K_2A' . BaA' 2aq. — CaA' (OH), 6aq. — AgA' : crystalline pp.

PHENYL-DIGUANIDE $C_6H_5N_4$, i.e. $NH_2C(NHPh).NH.C(NH_2).NH$ [c. 237°]. Formed by the action of alcoholic ammonia and $AgNO_3$ or $HgCl_2$ on guanyl-phenyl-thio-urea (Bamberger, *B.* 13, 1582). Formed also by heating aniline hydrochloride with di-cyan-di-amide in alcohol at 100° (Smolka u. Friedrich, *M.* 9, 232). Plates, v. sol. water and alcohol; absorbs CO_2 from air. When boiled with baryta-water it yields NH_3 , aniline, phenyl-urea [147°], phenyl-guanidine, guanidine, and urea (Emich, *M.* 12, 15). — $B'HCl$: prisms. Yields phenyl-carbamide when warmed with alcoholic potash and $CHCl_3$.

Salts.— $B'HNO_3$. — $B'H_2SO_4$. — $Cu(C_6H_5N_4).14aq$: red powder, sol. hot water. — $CaA'.H_2Cl_2.14aq$. — $CaA'.H_2SO_4.14aq$. — $CaA'.H_2CrO_4$. — NiA' . — $NiA'.H_2Cl_2$. — $NiA'.H_2SO_4.14aq$. — $CoA'.14aq$. $CoA'.H_2Cl_2.14aq$. — $CoA'.H_2SO_4$ aq: crimson needles.

(a) **Di-phenyl-guanidine** $C_{12}H_{10}N_4$, i.e. $NPh.C(NHPh).NH.C(NH_2).NH$. Formed by the action of $AgNO_3$ and aniline on guanyl-phenyl-thio-urea (Bamberger, *B.* 13, 1581). White solid, m. sol. water and alcohol, alkaline in reaction. — $B'HNO_3$. [231°]. White needles.

(b) **Di-phenyl-guanidine**
 $NH_2C(NPh).NH.C(NH_2).NH$ [c. 162°]. Formed by heating diphenylamine hydrochloride with di-cyan-di-amide (Emich, *M.* 12, 21). Thin needles, with alkaline reaction. — $B'HNO_3$. [203°]. Prisms. — $B'H_2SO_4$.

Tri-phenyl-guanidine $C_{18}H_{14}N_4$. [139°]. Formed from guanyl-tri-phenyl-thio-urea, NH_2 , and $AgNO_3$. Formed also from di-phenyl-guanidine and phenyl-cyanamide [78°] in ether (Rathke u. Oppenheim, *B.* 23, 1672). Prisms (from alcohol). With CS_2 at 100° it yields tri-phenyl-thio-ammeline $C_{18}H_{14}N_4S$. — $B'HCl$: prisms, v. sol. alcohol. — $B'H_2PtCl_6$.

PHENYL-GUANIDINE $C_6H_5N_3$, i.e. $NH_2C(NH_2)(NHPh)$. Formed by desulphuration of phenylthio-urea in presence of alcoholic NH_3 (Feuerlein, *B.* 12, 1802). Formed also by the action of baryta-water on phenyl-guanidine

(Emich, *M.* 12, 11). Decomposes on standing into phenylcyanamide and ammonia. — *Picrate* $B'C_6H_5N_3O_7$. [208°–214°] (Prelinger, *M.* 13, 99).

Di-phenyl-guanidine $C_{12}H_{10}N_4$, i.e. $NH_2C(NHPh)_2$. *Melaniline*. [147°]. S. (90 p.c. alcohol) 9–25 at 21°.

Formation.—1. From aniline and $CyCl$ or $CyBr$ (Hofmann, *A.* 67, 129; 74, 8; Weith a. Ebert, *B.* 8, 912).—2. By the action of PbO on a solution of di-phenyl-urea in alcoholic NH_3 (Hofmann, *B.* 2, 452, 688; Weith, *B.* 7, 937; Rathke, *B.* 12, 772).—3. By boiling phenyl-thio-urea with $HgCl(NHPh)$ and alcohol (Forster, *B.* 7, 291; *A.* 175, 35).—4. Together with thio-urea, by the action of aniline on mercuric fulminate (Steiner, *B.* 7, 1244; 8, 518).—5. By combination of di-phenyl-cyanamide with NH_3 (Weith, *B.* 7, 10).

Properties.—Monoclinic prisms (Arzruni, *P.* 152, 281), s. sol. cold water.

Reactions.—1. AcO at 100° yields acetyl-phenyl-urea [188°]. At 150° the product is acetyl-di-phenyl-urea [115°] (McCrath, *B.* 8, 1131).—2. *Phenyl thiocarbimide* forms, in the cold, $NHPh.CS.NPh.C(NH).NHPh$ [150°], a weak base, sl. sol. benzene. —3. $HClAq$ at 250° forms CO_2 , NH_3 , and aniline.—4. *Cyanogen* passed into its alcoholic solution forms $C_{12}H_{10}N_4$, which crystallises from alcohol in yellowish needles [154°], decomposed by $HClAq$ into crystalline melanoximide $C_{12}H_{10}N_4O_2$, which is split up by alcoholic potash into oxalic acid and diphenylguanidine, and by alcoholic HCl into NH_3 and di-phenyl-parabanic acid.

Salts.—The hydrochloride is gummy. — $B'HAuCl_4$: golden needles. — $B'HI.PtCl_6$. — $B'HI.Br$: stellate groups of needles, v. sol. water. — $B'HI$. — $B'HNO_3$. — $B'AgNO_3$: globules. — $B'H_2SO_4$: stellate groups of plates. — $B'HC_2O_4$. —*Sulphocyanide*: [115°]; m. sol. water.

Di-benzoyl derivative $C_{20}H_{14}N_4O_2$. [102°]. Monoclinic (McCrath, *B.* 8, 383).

Tri-phenyl-guanidine $C_{18}H_{14}N_4$, i.e. $NPh.C(NHPh)_2$. Mol. w. 287. [143°]; [147°] (F. u. W.). S. (alcohol) 4–5 at 0°.

Formation.—1. By adding I to an alcoholic solution of di-phenyl-thio-urea alone or mixed with aniline (Hofmann, *B.* 2, 453).—2. From di-phenyl-thio-urea and $HgCl(NHPh)$ (Forster, *B.* 7, 291).—3. From di-phenyl-cyanamide $C(NPh)_2$ and aniline (Weith, *B.* 7, 10).—4. Together with phenyl-thiocarbimide by heating di-phenyl-cyanamide with di-phenyl-urea (Weith, *B.* 9, 810).—5. By boiling di-phenyl-urea with inverted condenser (Barr, *B.* 13, 1765).—6. By heating di-phenyl-thio-urea with aniline, with Cu , or with $PbCl_2$ (Merz a. Weith, *Z.* [2] 4, 513, 609; 5, 583, 659; Girard, *Bl.* [2] 46, 506), or with $HgCl_2$ at 145° (Buff, *B.* 2, 498).—7. By heating di-phenyl cyanamide (2 mols.) with phenylene-o-diamine (1 mol.) at 210° (Keller, *B.* 24, 2505).—8. By the action of aniline on CCl_4 or chloropierin (Hofmann; Basset, *C.* 18, 31).—9. By the action of PCl_5 (1 mol.) on a mixture of di-phenyl-urea (3 mols.) and aniline (3 mols.).—10. By the action of PCl_5 (2 mols.) and CO_2 (3 mols.) on aniline (9 mols.) at 170° (Merz a. Weith, *Z.* [2] 6, 160).—11. By fusing di-phenyl-urea with $NaOH$ (Hentschel, *J. pr.* [2] 27, 500).

12. From phenyl thiocarbimide by chlorinating

(Py. 3) methyl-quinoline and phenyl-hydrazine (Ephraim, B. 24, 2820).

PHENYL-HYDRAZIDO-METHYL-THIAZOLE. Dihydride $C_8H_{12}N_2S$ i.e.

$CHMe.S$
 $CH_2-N \gg C.NH.NHPh$. Phenyl-propylene- ψ -thio-semicarbazide. [93°]. Formed by heating phenyl-allyl-thio-urea with conc. HClAq at 100° (Arenarius, B. 24, 269). Yellowish plates (from ligroin).—B'HCl. [202°]. Concentric crystals. —Pierac. [167°].

PHENYL-HYDRAZIDO-PHENYL-ACETIC ACID $C_8H_7N_2O_2$ i.e. $NHPh.NH.CHPh.CO_2H$. [158°]. Got by reducing the phenyl-hydrazide of phenyl-glyoxylic acid (Elbers, A. 227, 315). Crystalline, v. sl. sol. cold water, v. sol. alcohol.

PHENYL-HYDRAZIDO-PROPIONIC ACID $C_8H_7N_2O_2$ i.e. $NHPh.NH.CHMe.CO_2H$. [187°]. Formed by boiling its amide with NaOHaq (Reissert, B. 17, 1454; 20, 310; 22, 221). The ether is got by heating lactic ether with phenyl-hydrazine. Needles. Yields phenyl-amido-propionic acid on reduction.

Ethyl ether EtA'. [116°].—EtA' HCl.

Nitrile. [58°]. Formed by heating

$CH_3.CH(OH).CN$ with phenyl-hydrazine at 100°.

Amide. [124°]. White crystals.

Phenyl-hydrazido-propionic acid $NHPh.NH.CHMe.CO_2H$. [172°]. Formed by reducing the phenyl-hydrazide of pyruvic acid with sodium-amalgam (Fischer, A. Jourdan, B. 16, 2244; Japp a. Klingemann, B. 20, 3281; A. 247, 211). Needles (from MeOH). Re-oxidised by cold Fehling's solution to $NHPh.N.CMe.CO_2H$.

PHENYL-HYDRAZIDO-QUINOLINE $C_8H_7N_3$. [191°]. Formed from (Py. 3)-chloro-quinoline and phenyl-hydrazine (Ephraim, B. 24, 2818). Needles, v. sol. chloroform. Reduced by HI and P to (Py. 3)-amido-quinoline.

PHENYL-HYDRAZINE $C_8H_7N_2$ i.e. $NHPh.NH_2$. [23°]. (241.5° i.v.) at 750 mm. S.G. 1.097 (E. Fischer, A. 236, 198). H.C.v. 805,240. H.C.p. 806,300. H.F. 34,200 (from diamond) (Petit, A. Ch. [6] 17, 168).

Formation.—(E. Fischer, B. 8, 589, 1005, 1641; 9, 111, 880; A. 190, 67).—By the action of zinc and HOAc on diazo-benzene anilide or diazo-benzene diethylamide.

Preparation.—1. A cold solution of 7½ pts. of sodium nitrite in 50 pts. of water is slowly added to a well-cooled mixture of 10 pts. of aniline and 200 pts. of HCl (30 p.c.). To the diazo-benzene chloride solution so prepared a cold solution of 45 pts. of stannous chloride in 45 pts. of HCl is now added, when the mixture immediately becomes a thick magma of phenyl-hydrazine hydrochloride, which is filtered off, basified, and distilled (Meyer a. Lecco, B. 16, 2976).—2. Aniline (28 g.) is dissolved in K.CQ. (21 g.) and water (500 c.c.) by passing in SO_2 . The solution is mixed with a cold solution of $NaNO_2$ (25 g.) exactly neutralised by HOAc. After two hours the product is warmed till dissolved, acidified by HOAc, and reduced with zinc-dust and HClAq (Reychler, B. 20, 2468). By adding diazo-benzene nitrate to a cold aqueous solution of $KHSO_5$, heating the resulting $C_6H_5.N_2.SO_3K$ with excess of $KHSO_5$, and decomposing the $C_6H_5.NH.NH.SO_3K$, thus formed, by heating with HClAq.

Properties.—Oil, solidifying to monoclinic tables; v. sl. sol. hot water, almost insol. KOHAq. Miscible with alcohol, ether, benzene, and $CHCl_3$. Volatile with steam. Reduces Fehling's solution in the cold, N, aniline, and benzene being formed. When heated for a long time at 150° it is gradually split up into aniline, NH_3 , benzene, and N (Reissert a. Kayser, B. 23, 3703). Reduces SeO_2 to Se (Hinsberg, A. 260, 42). Gives benzene and N when boiled with $CuSO_4$. It is very poisonous.

Reactions.—1. H_2O forms benzene and diazo-benzene imide PhN_2 (Wurster, B. 20, 2633).—2. Yellow HgO added to its ethereal solution forms aniline, N, and $HgPh_2$ (Fischer, A. 199, 320). HgO added to a solution of the sulphate forms diazo-benzene sulphate and imide.—3. $SOCl_2$ in ether forms in the cold $NPh.N:SO$, which crystallises in yellow prisms [103°]; v. sol. ether, v. platine with steam. Thionyl-phenyl-hydrazine is hardly attacked by HCl, but is converted by NaOHaq into phenyl-hydrazine and Na_2SO_3 . Br forms $NPh.Br.NBr$. AcCl forms diazo-benzene chloride, S, and $HIOAg$ (Michaelis, B. 22, 2228; A. 270, 115).—4. SO_2 passed into an ethereal solution of phenyl-hydrazine forms $NHPh.NH.SO_2$ as a crystalline pp. SO_2 passed into an alcoholic solution of phenyl-hydrazine forms ($NHPh.NH$). SO_2 ; v. sol. water and alcohol, ig. sol. ether, crystallising in tables which shrink together at 70°, but decompose at a higher temperature (Michaelis a. Ruhl, B. 23, 471). SO_2 passed into a benzene solution at 75° forms $NHPh.N:SO$, which when heated with phenyl-hydrazine gives Ph_2S_2 , benzene, and N.—5. Dry CO_2 forms solid phenyl-hydrazine phenyl-carbazate ($NHPh.NH$). CO_2 or $N_2Ph.H.CO.O.N.PhH$, which is crystalline; sl. sol. water and ether, decomposed by hot water.—6. CS_2 forms the corresponding $NPh_2.CS.S.N_2PhH$ [97°], which at 110° splits up into H_2S and di-phenyl-thiocarbazine. COS forms crystalline $COS(N.H_2Ph)_2$ (Fischer, B. 22, 1935).—7. *Zinc-dust* and conc. HClAq slowly for aniline and NH_3 .—8. Excess of phenyl-hydrazine acts upon iodine, forming HI, aniline, and PhN_2 (Fischer, B. 10, 1835). Excess of I forms iodo-benzene, N, and HI (E. von Meyer, J. pr. [2] 36, 115). This reaction may be used for the volumetric estimation of phenyl-hydrazine.—9. Sulphur above 80° forms aniline, H_2S , N, Ph_2S_2 , Ph_2S , PhSH, benzene, and NH_3 .—10. Nitrous acid forms PhN_2 . KNO_2 added to the hydrochloride at 0° forms a yellow crystalline pp. of $NPh(NO)NH_2$.—11. Alcoholic potash and chloroform form, on heating, $C_8H_{12}N_2$ [180°], mol. w. 236. This body crystallises in white needles; sol. alcohol, scarcely affected by HClAq at 200°, and yielding crystalline $C_8H_7N_2.NO_2$ and $C_8H_7N_2.SO_3H$ (Ruhemann a. Elliott, C. J. 53, 850).—12. EtBr forms $NPhEt.NH_2$, $NPhH.NHEt$, and $NPhEt.Br.NH_2$.—13. Aqueous diazo-benzene nitrate added to a cold solution of the hydrochloride ppts. PhN_2 , aniline nitrate remaining in solution.—14. Reacts with aldehydes and ketones, forming phenyl-hydrazides; e.g. (Fischer, B. 17, 572) $CH_3.CHO + NPhH.NH_2 = H_2O + CH_3.CH:N.NHPh$. Thus a solution of phenyl-hydrazine hydrochloride (2 pts.) and crystallised sodium acetate (3 pts.) in water (20 pts.) gives a pp. of the phenyl-hydrazide when added to an aqueous solution of an aldehyde or ketone, either in the cold, or, in the case

of aromatic compounds, on warming. These phenyl-hydrazides are decomposed by acids into the original components, and, in alcoholic solution, by sodium-amalgam and HOAc into aniline and a base. The phenyl-hydrazides of ketones are converted by ZnCl_2 into derivatives of indole. The phenyl-hydrazides of aldehydes and ketones are described under the aldehydes and ketones from which they are derived.—15. *Diketones* containing the group CO.CHX.CO yield derivatives of phenyl-pyrazole. Saturated γ -diketones in etheral solution usually form a mono- or di-phenyl-hydrazide; in HOAc the product is the anhydride of the mono-phenyl-hydrazide, a derivative either of $\text{CH}_2\text{CH:N}$ or of CH:CH N.NHPh (Klingemann, *A.* 269, 108).—16. *Acetoacetic ether* forms a phenyl-hydrazide, which at 140° changes to oxy-phenyl-methyl-pyrazole $\text{NPh} \left\langle \begin{smallmatrix} \text{CO.CH} \\ \text{N:CMc} \end{smallmatrix} \right\rangle$ by loss of alcohol. *Acetyl-propionic acid* forms the compound $\text{CH}_2\text{C(N.HPh).CH}_2\text{CH}_2\text{CO}_2\text{H}$ [108]. *Benzoylacetic ether* forms two compounds [132] and [165] (Bender, *B.* 21, 2495).—17. *Reacts with sugars* as with aldehydes; thus a solution of glucose gives $\text{CH(OH).CH(OH).CH:N.HPh}$ [145] on heating with phenyl-hydrazine, while galactose gives $\text{C}_6\text{H}_{12}\text{O}_5\text{(N.HPh)}$ [158] (Fischer, *B.* 20, 824). On heating these compounds with aqueous phenyl-hydrazine acetate at 100° 'osazones' are formed, e.g. phenyl-glucosazone $\text{CH}_2\text{OH.CH(OH).C(N.HPh).CH:N.HPh}$ [204] and the isomeric phenyl-galactosazone [c. 191].—18. By heating with phenyl-hydrazine hydrochloride and NaOAc *arabinose* is converted into $\text{C}_5\text{H}_7\text{N}_2\text{O}_5$ [158]; *formose* into $\text{C}_5\text{H}_7\text{N}_2\text{O}_5$ [c. 144]; *arose* (the product of the action of NaOHAq on glyceric aldehyde) into $\text{C}_5\text{H}_7\text{N}_2\text{O}_5$ [c. 217] and an isomeride [159].—19. Phenyl hydrazine acetate reacts with the product of oxidation of glycerin with $\text{Na.CO}_2\text{Aq}$ and Br forming glycerosazone $\text{C}_5\text{H}_7\text{N}_2\text{O}_5$ crystallising from benzene in yellow plates [131] (Fischer a. Tafel, *B.* 20, 1089, 3386).—20. *Erythrite*, after oxidation by dilute HNO_3 , yields with phenyl-hydrazine hydrochloride and NaOAc the compound $\text{C}_5\text{H}_7\text{O}_5\text{(N.HPh)}_2$ [167].—21. *Mannite* on oxidation with HNO_3 yields levulose (mannitose) and mannose, which with phenyl-hydrazine forms $\text{C}_5\text{H}_7\text{N}_2\text{O}_5$ [195-200] (Fischer, *B.* 21, 1805).—22. The acetate reacts with the product of oxidation of dulcific by bromine and $\text{Na.CO}_2\text{Aq}$ with formation of the 'phenylidulcitosazone' $\text{C}_5\text{H}_7\text{N}_2\text{O}_5$ [206].—23. *Isodulcitol* heated with phenyl-hydrazine hydrochloride and sodium acetate at 100° forms 'phenyl-isodulcitol-osazone' $\text{C}_5\text{H}_7\text{N}_2\text{O}_5$ or $\text{C}_5\text{H}_{10}\text{O}_5\text{(N.HPh)}_2$ [180]. Solutions of *isodulcitol* and phenyl-hydrazine form, on mixing, $\text{C}_5\text{H}_7\text{O}_5\text{(N.HPh)}$ [159] (Fischer a. Tafel, *B.* 20, 2574; Raymann, *Bl.* [2] 47, 760).—24. *Sorbin* heated with aqueous phenyl-hydrazine hydrochloride and NaOAc at 100° forms the osazone $\text{C}_5\text{H}_7\text{N}_2\text{O}_5$ [164].—25. *Milk sugar* heated with aqueous phenyl-hydrazine hydrochloride and NaOAc forms $\text{C}_5\text{H}_7\text{N}_2\text{O}_5$ [200] and $\text{C}_5\text{H}_7\text{N}_2\text{O}_5$ [224].—26. *Maltose* forms $\text{C}_5\text{H}_7\text{N}_2\text{O}_5$ [191].—27. The acetate gives with *glycolic, phenyl-glycolic, and pyruvic acids* the corresponding phenyl-hydrazides [137], [153], and [192] respectively.—28. Phenyl-

hydrazine in HOAc (50 p.c.) gives with a dilute solution of *gluconic, galactonic, and arabinose carboxylic acids* compounds $\text{C}_6\text{H}_{11}\text{O}_5\text{N}_2\text{HPh}$ [200], [203], and [216] respectively (Fischer a. Passmore, *B.* 22, 2760). These compounds are m. sol. hot water. *Saccharic acid* gives a similar compound $\text{C}_6\text{H}_{11}\text{O}_5\text{N}_2\text{HPh}$ [165] which, as well as the compounds from mucic and metasaccharic acid, is almost insoluble. The compound from mucic acid melts at 240° . All these compounds contain the group CO.NH.NHPh . Compounds containing this group are also obtained by the action of phenyl-hydrazine and dilute HOAc at 100° on *formic, succinic, malic, tartaric, cinnamic, and gallic acids*, but not from *glycolic, lactic, and glyceric acids*. The compounds go from succinic, malic, gallic, and tartaric acid melt at 218° , 223° , 187° , and 240° respectively. Acetyl-phenyl-hydrazine is produced when aqueous phenyl-hydrazine acetate is heated at 130° ; and a similar reaction occurs with benzoic, glyceric, and lactic acids. Compounds containing the group CO.NH.NHPh give a reddish-violet colouration with H_2SO_4 and a little FeCl_3 , and they are readily decomposed by KOHAq and by baryta into phenyl-hydrazine and a salt of the acid (Fischer, *B.* 22, 2728).—29. *Glucose carboxylic lactone* yields $\text{C}_5\text{H}_{13}\text{O}_5\text{N}_2\text{HPh}$ [172], while *mannose carboxylic acid* gives an isomeric body [223].—30. The acetate gives with *rhamnose carboxylic acid* the compound $\text{C}_5\text{H}_{13}\text{O}_5\text{N}_2\text{HPh}$ [c. 210], while *malonic acid* heated at 100° with phenyl-hydrazine and dilute HOAc forms $\text{C}_5\text{H}_7\text{N}_2\text{O}_5$ [143] and $\text{CO}_2\text{H.CH}_2\text{CO.N.HPh}$ [154], which when heated with water and phenyl-hydrazine at 200° yields $\text{CH}_2\text{CH(CO)} \text{N.HPh}$ [128].—32. *Lactic ether* forms, on heating, phenyl-hydrazido-propionic ether. *a-Oxy-butyric acid* at 160° forms $\text{C}_5\text{H}_{11}\text{N}_2\text{O}_5$ [152], while *mandelic acid* yields $\text{C}_5\text{H}_{11}\text{N}_2\text{O}_5$ [182] (Reissert a. Kayser, *B.* 22, 2924).—33. *gamma-Oxy-valeric lactone* at 100° forms $\text{C}_5\text{H}_9\text{O}_5\text{N}_2\text{HPh}$ [79] (Vislicenus, *B.* 20, 402).—34. *Benzyl-carbinol* gives N.HPh:CPh.CH(OH) [112] and the 'osazone' $\text{N.HPh:CPh.CH:N.HPh}$ [192] (Laubmann, *A.* 243, 244).—35. Boiling aqueous *itaconic acid* forms the acid $\text{NHPh.N} \left\langle \begin{smallmatrix} \text{CH}_2\text{CH.CO}_2\text{H} \\ \text{CO} \end{smallmatrix} \right\rangle$ [194] (Scharfenberger, *A.* 254, 150).—36. *Cinnamic acid* forms $\text{C}_5\text{H}_7\text{N}_2\text{O}_5$ [183], which on distillation yields $\text{C}_5\text{H}_7\text{N}_2\text{O}_5$ [251] (Knorr, *B.* 20, 1107).—37. *Acrolein* reacts forming phenyl-pyrazole dihydride $\text{NPh} \left\langle \begin{smallmatrix} \text{N:CH} \\ \text{CH}_2\text{CH}_2 \end{smallmatrix} \right\rangle$ [52] (274) (Fischer a. Knoevenagel, *A.* 239, 194).—38. *Mesityl oxide* yields phenyl-tri-methyl-pyrazole $\text{NPh} \left\langle \begin{smallmatrix} \text{N} \\ \text{CMc} \end{smallmatrix} \right\rangle$ (F. a. K.).—39. *Chloro-acetone* in alcoholic solution at -18° forms $\text{C}_5\text{H}_7\text{N}_2$ [158] which yields an acetyl derivative $\text{C}_5\text{H}_7\text{AcN}_2$ [220] (Bender, *B.* 21, 2496). *s-Tetra-chloro-acetone* forms $\text{C}_5\text{H}_7\text{N}_2$ [126] converted by fuming HNO_3 into $\text{C}_5\text{H}_7\text{N}_2\text{O}_5$ [235] and by SnCl_4 to two bases $\text{C}_5\text{H}_7\text{N}_2$ [77] and [193] (Levy a. Witte, *A.* 252, 343; Zincke a. Kegel, *B.* 22, 1478).—40. *Tetra-bromo-di-benzyl-ketone* heated with alcoholic phenyl-hydrazine at 150° forms $\text{C}_5\text{Ph}_2\text{(N,Ph)}$ [70] (Bourcart, *B.* 22, 1369).—41. *Di-bromo-aceto*

phenone forms $N_2HPh:CPh.CH:N_2HPh$ [148°], crystallising from alcohol in yellow prisms (B.).

42. *Bromo-acetyl-propionic ether* mixed with an alcoholic solution of phenyl-hydrazine forms $CH_2C(N_2HPh).CH:CH.CO.Et$ [117-5°], which on reduction with tin and HCl forms methyl-indole carboxylic acid (Bender). Bromo-acetyl-propionic acid forms $CH_2C(N_2HPh).CH:CH.CO_2H$ [157°] (Decker, B. 21, 2937). — 43. *Di-chloro-maleic imide* at 100° forms $C_6O_2(N_2H_2Ph)_2NH$ crystallising from acetone in orange-red needles (Ciamician, B. 22, 2495). — 44. *Amides* react thus: $N_2H_2Ph + R.CO.NH_2 = NH_2 + R.CO.N_2H_2Ph$ (Just, B. 19, 1201). — 45. *Carbanic ether* forms, on heating, di-phenyl-carbazide $CO(NH.NH.NH)_2$ [151°] (Skinner a. Ruhemann, B. 20, 3372). — 46. Reduces *alloxan* to *alloxantin*, N and benzene being formed (Pellizzari, G. 17, 254). In this reaction the first product is the compound $CO \begin{smallmatrix} NH.CO \\ NH.CO \end{smallmatrix} C(OH).N_2H_2Ph$ (Skinner a. Ruhemann, C. J. 53, 550). — 47. *Parabanic acid* with phenyl-hydrazine hydrochloride and NaOAc yields $C_{12}H_{12}N_2O$ [170°], which on boiling with water forms $NH_2.CO.NH.CO.CO.N_2H_2Ph$ [115°] (S. a. K.). — 48. *Urea* heated with phenyl-hydrazine hydrochloride at 160° forms phenyl-urazole $NPh \begin{smallmatrix} NH.CO \\ CO.NH \end{smallmatrix}$ [263°]. — 49. Reduces *nitroso-aniline* to *p*-phenylene-diamine and $C_2H_2N_2O$ (Fischer, B. 21, 2610). — 50. The acetate (2 mols.) acting on *nitroso-dimethyl-aniline* (3 mols.) forms $C_{12}H_{12}N_2O$ [103°]. An ethereal solution of phenyl-hydrazine converts nitroso-di-methyl-aniline into di-methyl-amido-benzene-azo-di-methyl-aniline and phenylene-di-methyl-diamine. In alcoholic solution there is formed $NHPh.C_2H_4.NMe_2$ [130°] which yields a nitrosamine $C_2H_4.N_2O$ [116°] (O. Fischer, B. 21, 2609). — 51. *Di-nitroso-acetone* (1 mol.) mixed with phenyl-hydrazine (1 mol.) in hot alcoholic solution forms $CH(OH).C(N_2HPh).CH(OH)$ [145°]. Di-nitroso-acetone boiled with excess of phenyl-hydrazine acetate forms $C_6H_2N_2$ crystallising in yellow plates [122°]. — 52. *Diazo-acetic ether* at 100° gives off N and forms a colourless compound [136°]. — 53. *p*-Diazobenzene sulphonic acid forms the compound $N_2C_6H_4.SO_3N_2H_2Ph$ crystallising in plates (Griess, B. 20, 1528). — 54. *Di-acetyl-succinic ether* fused with phenyl-hydrazine at 100° forms $CO.Et.CH(CMe:N.PhH).CHAc.CO.Et$ [91°] and $CO.Et.CH(CMe:N.PhH).CH(CMe:N_2PhH).CO.Et$ which on heating with toluene at 180° gives di-oxy-di-phenyl-di-methyl-dipyrzyl (q.v.). — 55. *Dioxims* form additive compounds; e.g. *glyoxim* yields $C_2H_2(OH).N_2H_2Ph$ [110°], *di-phenyl-glyoxim* yields $C_2Ph_2(OH).N_2H_2Ph$ [150°], while the *di-oxim* of (β)-naphthoquinone forms $C_{12}H_8(OH).N_2H_2Ph$ [138°] (Polonowsky, B. 21, 182). — 56. *Phloroglucin* kept for five days with an alcoholic solution of phenyl-hydrazine in the cold forms $C_6H_3(OH)(N_2H_2Ph)_2$ [144°] which may be oxidised by FeCl₃ to $C_6H_2(OH)(N_2Ph)_2$ [177°] (Baeyer B. 22, 2891). — 57. *Thio-acetoacetic ether* forms $S(CH \begin{smallmatrix} CO-NPh \\ CMe:N \end{smallmatrix})_2$ [183°], together with the compounds $NHPh.N:C \begin{smallmatrix} CO-NPh \\ CMe:N \end{smallmatrix}$ [156°], $S_2(CH \begin{smallmatrix} CO-NPh \\ CMe:N \end{smallmatrix})_2$ and di-oxy-di-phenyl-di-

methyl-dipyrzyl (Sprague, C. J. 59, 332). — 58. *Cyanogen* passed into an emulsion of phenyl-hydrazine in cold water forms the dicyanide (i. infra). — 59. *Cyanogen* passed into an alcoholic solution forms $PhN.H_2C(NH).C(NH).N.PhH$ [225°], crystallising in white plates (from alcohol). The same compound is formed by the action of phenyl-hydrazine on cyananiline. I gives a rose-red colour with alcoholic NH₄Cl. Conc. H₂SO₄ is coloured indigo-blue. Dry HCl forms the hydrochloride $C_6H_5N_2HCl$ [188°]. Dilute HCl forms $PhN.NH.CO.C(NH).NH.NHPh$ [180°]. — 60. *Cyananiline* in chloroform solution forms, after boiling, matted needles of the compound $C_{12}H_{12}N_2Cl_2$ [200°-212°]. This body is perhaps $(PhH.N_2CHCl.C_6H_5N_2)2HCl$ (Sent J. pr. [2] 35, 533). — 61. PCl₅ in ether forms amorphous $NHPh.N:P.NH.NHPh$ converted by water into $(NHPh.NH).POH$, a yellowish-white powder [92°] which reduces Fehling's solution in the cold (Michaelis a. Oster, A. 270, 126). This body is split up by acids into phenyl-hydrazine and H₃PO₄, but is attacked by alkalis with difficulty. Benzoic aldehyde produces $NPhH.N:CHPh$ and H₃PO₄. — 62. POCl₃ forms $PO(NH.NHPh)_2$ [196°], easily decomposed by acids and alkalis (Michaelis, A. 270, 135). — 63. PSCl₃ forms, in like manner, $PS(NH.NHPh)_2$ [154°]. — 64. AsCl₃ forms $(N_2H_2Ph)_2AsCl$, an amorphous powder decomposed at 235°. — 65. BCl₃ forms, in like manner, $(N_2H_2Ph)_2BCl$, v. sol. water, decomposed at 242°. — 66. C₂H₅PCl₂ in ether forms $NHPh.N.PC_2H_5$ [152°] crystallising from EtOAc in plates (Michaelis a. Oster, A. 270, 129). It reduces hot Fehling's solution, and is split up by acids into $PhPO_2H_2$ and phenyl-hydrazine.

Salts.—B⁺HCl. Plates, m. sol. water. Got by ppg. an alcoholic solution of the base by HCl, and washing the pp. till it is colourless. — B⁺HBr. Needles (from water). — B⁺H₂SO₄. Plates, v. sol. water. — B⁺C₂H₅NO₂. Yellow needles. — B⁺H₂CO₃. Plates. — Benzene sulphinate; [131°] (Eseales, B. 18, 895). — Di-nitro-(α)-naphthol sulphinate: light-brown needles, sl. sol. hot water (Richardson, C. N. 58, 39). — Sulphocyanide: sparingly soluble plates. Changes at 160°-170° into phenyl-thio-semicarbazide. — B⁺H₂PO₄. [118°] (Michaelis, A. 270, 127, 133). — B⁺H₂PO₃. [121°]. — B⁺C₂H₅PH₂O₂. [135°].

Sodium derivative $C_6H_5NNa.NH_2$. Formed by dissolving 8 g. of sodium in 70 g. of warm phenyl-hydrazine. The H evolved reduces some of the phenyl-hydrazine to NH₂ and aniline; when the reaction is complete the aniline and excess of phenyl-hydrazine are distilled off by heating the product in an oil-bath to 200°-210° (not higher) in a current of H₂. It is a yellow hygroscopic powder. When finely divided it sometimes takes fire in the air. Decomposed by water into phenyl-hydrazine and NaOH. Readily reacts with alkyl haloids, giving unsymmetrical phenyl-alkyl-hydrazines (Michaelis, B. 19, 2448; A. 252, 266).

Formyl derivative $NHPh.NH.CHO$. [145°]. Formed by heating formamide with phenyl-hydrazine at 180°. White scales.

Acetyl derivative $NHPh.NH.Ac$. [128-6°]. Formed by heating phenyl-hydrazine with EtOAc or acetamide (Fischer, A. 190, 129; Just, Z.

19, 1201). Formed also from the sodium-derivative and Ac_2O at 0° (Michaelis a. Schmidt, *A.* 252, 301). Six-sided prisms, sl. sol. cold water.

Di-acetyl derivative NPhAc.NHAc . [108°]. Formed from NPhNa.NH_2 and AcCl in ether. Tables or needles, v. c. sol. alcohol. Completely reduces hot Fehling's solution.

Chloro-acetyl derivative $\text{NPhPh.NH.CO.CH}_2\text{Cl}$. [115°]. Formed from the base and $\text{CH}_2\text{Cl.COCl}$ in ether (Gattermann, *B.* 25, 1081).

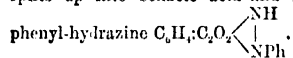
Propionyl derivative NPhPh.NH.CO.Et . [158°] (Freund a. Goldschmidt, *B.* 21, 2161).

n-Butyryl derivative. [114°]. Scales, v. sol. ether (Michaelis a. Schmidt, *A.* 252, 308).

Isovaleryl derivative $\text{NPhPh.NH.CO.CH(CH}_3)_2$. [101°]. Formed from the base and aceto-valeric anhydride (Autenrieth, *B.* 20, 3190). Plates, v. sl. sol. cold ligroin.

Heptyl derivative. [117°]. Needles.

s-Benzoyl derivative NPhPh.NHBz . [169°]. Formed from phenyl-hydrazine by adding BzCl in ether at 0° (Fischer, *A.* 190, 125), or by heating with benzanide (Just, *B.* 19, 1203). Formed also by warming phenyl-hydrazine with BzCl (Hausknecht, *B.* 22, 329). Prisms, sl. sol. hot water. Yields NPhMe.NHBz on methylation. Reduces H_2O . Phthalic anhydride at 180° forms an addition-compound $\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}$ [172°], crystallising from alcohol in prisms. It is probably $\text{CO}_2\text{H.C}_6\text{H}_4\text{CO}_2\text{H.C}_6\text{H}_4\text{N.NHPh}$. At 250° it splits up into benzoic acid and (β)-phthalyl-



a-Benzoyl derivative NPhBz.NH_2 . [70°]. A product of the action of BzCl in benzene on NPhNa.NH_2 at 0° (Michaelis a. Schmidt, *B.* 20, 33, 1718; *A.* 252, 310). Needles (from water). Reduces hot Fehling's solution but not HgO . Conc. HCl at 160° gives HOBz and phenyl-hydrazine. HNO_3 forms in acid solution benzanilide and N_2O , but in neutral solution it forms N_2Ph and HOBz . Reacts like phenyl-hydrazine with aldehydes and ketones; thus acetone yields NPhBz.N:CMe , [115.5°], acetophenone forms NPhBz.N:CMcPh [124°], and benzoic aldehyde gives NPhBz.N:CHPh [123°]. Salts.— B^+HCl . [202°]. Needles, m. sol. HClAq .— NPhBz.NHNa . White pp., decomposed by water.— $\text{B}^+\text{H}_2\text{SO}_4$. [191°]. Needles, sl. sol. cold water.— B^+HNO_3 . [145°].— $\text{H}^+\text{C}_6\text{H}_5\text{N}_3\text{O}_2$. [122°].

Di-benzoyl derivative NPhBz.NHBz . [178°] (Fischer, *A.* 190, 128; M. a. S.). Prisms, v. sl. sol. water, sol. alkalis. On methylation it yields NPhBz.NHBz .— NPhBz.NBzNa : plates.

Benzoyl-acetyl derivative NPhBz.NHAc . [153°]. Got from NPhBz.NH_2 and Ac_2O . Needles (from dilute alcohol).

p-Nitro-benzoyl derivative $\text{NPhPh.NH.CO.C}_6\text{H}_4\text{NO}_2$. [198°]. Formed from phenyl-hydrazine and $\text{C}_6\text{H}_4(\text{NO}_2)\text{CN}$ (Hausknecht, *B.* 22, 329). Yellowish-red needles.

o-Amido-benzoyl derivative. [170°]. Got by warming phenyl-hydrazine with an alcoholic solution of isatoic acid (Meyer, *J. pr.* [2] 33, 20). Yellow needles, v. sl. sol. ether.

m-Amido-benzoyl derivative $\text{NPhPh.NH.CO.C}_6\text{H}_4\text{NH}_2$. [161°]. Formed by

heating phenyl-hydrazine (1 mol.) with *m*-amido-benzoic acid (1 mol.) at 165° (Pellizzari, *G.* 16, 200). Scales, insol. cold alkalis, sol. acids.

Amido-toluy derivative [8:6:1] $\text{C}_6\text{H}_3\text{Mo}(\text{NH}_2)_2\text{CO.NH}_2\text{Ph}$. [198°]. Formed from methyl-isatoic acid and phenyl-hydrazine (Pan-aotovitch *J. pr.* [2] 33, 68). Prisms (from chloroform), sl. sol. ether.

Phenyl-acetyl derivative $\text{N}_2\text{H}_2\text{Ph.CO.CH}_2\text{Ph}$. [169°]. Got by heating phenyl-acetic acid with phenyl-hydrazine at 150° (Bülow, *A.* 236, 196). Needles (from alcohol), sl. sol. water.

Cinnamoyl derivative $\text{N}_2\text{H}_2\text{Ph.CO.C}_6\text{H}_4\text{Ph}$. [258°]. Got by heating cinnamic acid with phenyl-hydrazine at 190° (Knorr, *B.* 20, 1708). Forms, on distillation, a compound $\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}$ [258°], crystallising in needles with green fluorescence.

Malyl derivative $\text{C}_6\text{O}_2(\text{N}_2\text{H}_2\text{Ph})_2$. [278°]. Described in vol. iii. p. 655.

Ethyl-malonyl derivative $\text{CHEt}(\text{CO.NH}_2\text{Ph})_2$. [233°]. Got by heating ethyl-malonic amide with phenyl-hydrazine at 220° (Freund a. Goldsmith, *B.* 21, 1242). Needles (from HOAc). Converted by COCl_2 into $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_4$ [113°].

Succinyl derivative $\text{C}_4\text{H}_4\text{C}_2\text{O}_2(\text{N}_2\text{H}_2\text{Ph})_2$. [218°]. Formed from succinyl chloride (1 mol.) and phenyl-hydrazine (2 mols.). Formed also by heating $\text{C}_4\text{H}_4\text{C}_2\text{O}_2\text{S}$ with phenyl-hydrazine and HOAc (Zanetti, *Rend. Accad. Linc.* [4] 5, i. 225). Plates (from HOAc) (Freund, *B.* 21, 2456; Fischer a. Passmore, *B.* 22, 2734). When succinic anhydride is heated with phenyl-hydrazine at 160° there is formed $\text{C}_4\text{H}_4\text{C}_2\text{O}_2\text{N.NHPh}$ [155°], which yields a nitrosamine $\text{C}_4\text{H}_4\text{C}_2\text{O}_2\text{N}_2\text{Ph.NO}$ [84°] (Hötte, *J. pr.* [2] 35, 293).

(a) **Phthalyl derivative** $\text{C}_6\text{H}_4\text{C}_2\text{O}_2\text{N.NHPh}$. [179°]. Formed from phenyl-hydrazine and phthalyl chloride in ether (Pickel, *A.* 232, 233). Formed also by heating phenyl-hydrazine (1 mol.) with phthalimide (1 mol.) at 120° (Pellizzari, *G.* 16, 203; Just, *B.* 19, 1204); or with phthalic anhydride (1 mol.) at 160° (Hötte, *J. pr.* [2] 33, 99; 35, 268). Prepared by boiling an alcoholic solution of phthalic anhydride with phenyl-hydrazine. Colourless needles (from alcohol), insol. water and alkalis. Conc. H_2SO_4 forms a violet solution, turning brown. **Reactions.**—1. Converted by boiling alcoholic potash into $\text{N}_2\text{H}_2\text{Ph.CO.C}_6\text{H}_4\text{CO}_2\text{H}$ [166°], an acid of which the benzoyl derivative $\text{NPhPh.NBz.CO.C}_6\text{H}_4\text{CO}_2\text{H}$ [172°] is formed by heating NPhPh.NHBz with phthalic anhydride at 180° .—2. Boiling aqueous KOH or HClAq at 160° splits it up into phthalic anhydride and phenyl-hydrazine.—3. **Benzoyl chloride** at 160° forms $\text{C}_6\text{H}_4\text{C}_2\text{O}_2\text{N.NHPhBz}$ [193°].—4. **Nitrous acid** passed into its solution in diluted HOAc forms the nitramine $\text{C}_6\text{H}_4\text{C}_2\text{O}_2\text{N.NPh.NO}_2$ [148°]; but in boiling HOAc it forms the di-nitro-derivative $\text{C}_6\text{H}_4\text{N}_2\text{O}_4$ [182°]. Nitrous acid passed into phthalyl-phenyl-hydrazine suspended in ether forms the nitrosamine $\text{C}_6\text{H}_4\text{C}_2\text{O}_2\text{N.NPh(NO)}$ [154°].—5. Alcoholic NH_3 at 80° forms unstable $\text{NH}_2\text{CO.C}_6\text{H}_4\text{CO.NH.NHPh}$ [146°], which decomposes at 170° into NH_3 and (β)-phthalyl-phenyl-hydrazine [210°].

(8) *Phthalyl derivative*

$C_6H_4C_2O_2 \begin{smallmatrix} \text{NH} \\ \text{NPh} \end{smallmatrix}$ [210°]. Formed at the same time as the (a)-isomeride by heating phenylhydrazine with phthalimide or phthalic anhydride, being the chief product when the temperature is above 163° (Pellizzari, *G.* 16, 204; 17, 278; Hütte, *J. pr.* [2] 35, 284). Monoclinic tables (from benzene) or prisms (from alcohol), v. sol. alkalis. Ammoniacal $AgNO_3$ ppts. $C_6H_4C_2O_2N_2PhAg$.

Reactions.—1. $NaOMe$ and MeI at 100° form $C_6H_4C_2O_2N_2PhMe$ [125°], which is decomposed by conc. $HClAq$ into phthalic acid and $NHPh.NHMe$.—2. $KOEt$ and EtI give $C_6H_4O_2N_2PhEt$ [106°].—3. $BzCl$ at 200° forms $C_6H_4O_2N_2PhAc$ [122°].

Phthalyl derivative

$C_6H_4(CO.NH.NHPh)_2$ [191°]. Formed by heating phenylhydrazine (2 mol.) with phthalic anhydride (1 mol.) at 150° (H.). White tables. At 170° it gives the (β)-phthalyl derivative [210°].

Nitrosamine $NH_2.NPh.NO$. Formed by adding $NaNO_2$ to an aqueous solution of phenylhydrazine hydrochloride at 0° (Fischer, *A.* 190, 92). Pale-yellow plates. Very poisonous. Converted by hot alcoholic potash into diazobenzene-imide. Alcoholic HCl acts in like manner. Exhibits Liebermann's reaction.

Dicyanide $C_6H_4N_4$, i.e.

$NH_2.NPh.C(NH).CN$? Separates as colourless flakes when cyanogen is passed into an emulsion of phenylhydrazine and cold water (Bladin, *B.* 18, 1544). Monoclinic laminae, v. sol. alcohol and ether. Decomposes above 160°. Yields a formyl derivative $C_6H_4(CHO)_2N_4$ [193°].

Reactions.—1. By heating with Ac_2O it is converted into $C_6H_4N_4$ [108°], which on saponification yields an acid $C_6H_4N_4O_2$ [177°], which on heating loses CO_2 , leaving only $C_6H_4N_4O$ (c. 240°).—2. By heating with *propionic anhydride* it is converted into $C_6H_4N_4$ [38°].—3. By treatment with *nitrous acid*, followed by boiling with water, it yields $C_6H_4N_4$, crystallising in needles [56°], v. sl. sol. water.—4. *Acetic aldehyde* in alcohol and HCl give $CH_3.CH:N.NPh.C(NH).CN$ [96.5°], crystallising in pale-yellow plates, v. e. sol. alcohol and ether, insol. water; converted by alcoholic $AgNO_3$ into phenyl-methyl-triazole carboxylic nitrile [109°] (Bladin, *B.* 25, 184).—5. *Benzoic aldehyde* forms the corresponding $CHPh:N.NPh.C(NH).CN$ [129.5°], crystallising from alcohol in prisms, oxidised by $FeCl_3$ to $C_6H_4N_4$ [156°] (Bladin, *B.* 22, 796).—6. *Pyruvic acid* in alcohol forms the above phenyl-methyl-triazole carboxylic nitrile on warming gently (Bladin, *B.* 19, 2598).—7. Boiling *acetoacetic ether* forms the compound $CO_2H.CH_2.CMe:N.NPh.C(NH).CN$ [209°], the oily ether of this acid, and phenyl-methyl-triazole carboxylic nitrile $N \begin{smallmatrix} \text{CMe} \\ \text{NPh.CCN} \end{smallmatrix}$ [109°] (Bladin, *B.* 25, 190). The acid forms the salts KA' and NH_4A' , and is converted by nitrous acid into $CO_2H.C(NOH).CMe:N.NPh.C(NH).CN$ [218°], and by potash into the compound $CO_2H.CH_2.CMe:N.NPh.CO.CN$ [188°], from which potassium nitrite and $HClAq$ form $CO_2H.C(NOH).CMe:N.NPh.CO.CN$ [209°].

References.—AMIDO-, IODO-, NITRO-, and OXY PHENYL-HYDRAZINE.

o-Di-phenyl-hydrazine $NPh_2.NH_2$ [34.5°] (220° at 40 mm.) (Stahel, *A.* 258, 243). Formed by reducing di-phenyl-nitrosamine $NPh_2.NO$ in alcoholic solution with zinc-dust and $HOAc$ (Fischer, *A.* 190, 174). Monoclinic tables (from ligroin), partially decomposed on distillation into diphenylamine and NH_3 . Conc. H_2SO_4 forms a deep-blue solution. Decomposed by nitrous acid into $NPh_2.NO$ and N_2O . Reduces H_2O , forming in the cold crystalline tetraphenyl-tetrazone $NPh_4.N:N.NPh_4$ [123°], but if the temperature rises the products are N and diphenylamine. Benzoic aldehyde forms $NPh_2.N:CHPh$ [122°]. With salicylic aldehyde, furfuraldehyde, glucose, mannose, galactose, and rhamnose it forms di-phenyl-hydrazides, melting at 139°, 90°, c. 162°, c. 155°, 147°, and 134° respectively.

Salts.— $BHCl$. Needles, v. sl. sol. cold water. — $B_2H_2SO_4$: needles, m. sol. dilute H_2SO_4 .

Formyl derivative $NPh_2.NH.CHO$ [116.5°]. Formed by boiling the formyl derivative of phenylhydrazine with ammoniacal $CaSO_3$ (Gattermann, *B.* 25, 1075). Needles, sl. sol. hot water and ligroin, v. sol. alcohol.

Acetyl derivative $NPh_2.NHAc$ [185°]. Formed by boiling $NHPh.NHAc$ with $HOAc$ and $Cu(OAc)_2$ (Tafel, *B.* 25, 413).

Propionyl derivative [178°]. Needles. *Benzoyl derivative* $NPh_2.NHbz$. [189°] (G.); [192°] (Fischer, *A.* 190, 175). Needles (from acetone), m. sol. alcohol.

Phthalyl derivative $C_6H_4O_2N_2.NPh_2$ [155°]. Formed by heating di-phenylhydrazine with phthalic anhydride at 160° (Hütte, *J. pr.* [2] 35, 271).

s-Di-phenyl-hydrazine $NHPh.NHPh$. *Hydrazobenzene*. Mol. w. 184. [131°]. $H.C.$ 1,598,000 (from diamond) (Petit, *C. Ch.* [6] 17, 163). $S.$ (alcohol) 5 at 16° (Moltschanowsky, *C. J.* 42, 965). Prepared by passing H_2S into a solution of azobenzene $Ph.N=N.Ph$ in alcoholic NH_3 (Hofmann, *Pr.* 12, 576). Formed also by reducing nitro-benzene with sodium-amalgam or zinc-dust (Alexejeff, *Z.* 1868, 497; Glaser, *A.* 142, 364). Lamine, sl. sol. water, m. sol. alcohol and ether. Yields aniline and azobenzene on distillation.

Reactions.—1. $HClAq$ converts it into the isomeric di-*p*-amido-diphenyl (benzidine), H_2SO_4 acts in like manner.—2. Readily oxidised to azobenzene, even by moist air.—3. *Nitrous acid*, passed into an alcoholic solution at 0°, yields a nitroso-compound which, when warmed, violently decomposes into NO and azobenzene (Bayer, *B.* 2, 683).—4. On heating with $BzCl$ it yields di-benzoyl-di-*p*-amido-diphenyl; formic acid gives di-formyl-di-*p*-amido-diphenyl (Stern, *B.* 17, 879); and phthalic anhydride yields di-phthalyl-di-amido-diphenyl (Bandrowski, *B.* 17, 1181).—5. Boiling *benzoic aldehyde* forms azobenzene, but benzoic aldehyde and $ZnCl_2$ gives $C_6H_4(N:CHPh)_2$ (Clève, *Bl.* [2] 45, 188). Benzoic aldehyde, heated with hydrazobenzene at 120°–150°, forms 'benzhydrazoin' $CHPh \begin{smallmatrix} \text{NPh} \\ \text{NPh} \end{smallmatrix}$ [55°]. The *o*-nitro-derivative $C_6H_4(NO_2).CHN \begin{smallmatrix} \text{NPh} \\ \text{NPh} \end{smallmatrix}$ of this body melts at 66°.—6. *Furfuraldehyde* forms

$C_6H_5O.CH \leftarrow \begin{smallmatrix} NPh \\ NPh \end{smallmatrix}$ [59°] (Cornelius a. Homolka, *B.* 19, 2240).—7. *Phenyl cyanate* (2 mols.) and some benzene at 150° forms the compound $NHPh.CO.NPh.NPh.CO.NHPh$ [220°] (Goldschmidt a. Rosell, *B.* 23, 490).

Acetyl derivative $NHPh.NPhAc$. [159°]. Formed from *s*-di-phenyl-hydrazine and $Ac.O$ in the cold (Stern, *B.* 17, 330). Needles (from alcohol). Decomposed by heat into acetanilide and azobenzene.

Di-acetyl derivative $NPhAc.NPhAc$. [105°]. Formed from *s*-di-phenyl-hydrazine and $Ac.O$ (Schmidt a. Schultz, *B.* 12, 485; *A.* 207, 326). Yellowish trimetric crystals (from alcohol); *ab:c* = 67:1:56, not affected by dilute $HClAq$.

Chloro-o-derivatives
 $C_6H_5.NH.NH.C_6H_4.Cl$. [90°].— $N_2H_4(C_6H_4.Cl)[1:3]$. [91°].— $N_2H_4(C_6H_4.Cl)[1:4]$. [122°] (Claus a. Heumann, *B.* 13, 1181, 19, 1688; Laubenheimer, *B.* 8, 1624).

Bromo-derivative $C_6H_5.NH.NH.C_6H_4.Br$. [115°]. Formed from benzene-azo-*p*-bromobenzene and alcoholic ammonium sulphide (Janowsky a. Erb, *B.* 20, 361). Tables. Converted by H_2SO_4 into bromo-benzidine.

Di-bromo-derivatives $N_2H_4(C_6H_4.Br)_2$. *o*. [82°]. *m*. [109°]. *p*. [130°] (J. a. E.; Gabriel, *B.* 9, 1406; Wergo, *A.* 165, 192).

Iodo-derivatives *v.* vol. iii. p. 41.

Nitro-derivatives *v.* vol. iii. p. 607.

Oxy-derivatives *v.* vol. iii. p. 743.

Chloro-nitro-derivative
 $NHPh.NH.C_6H_4.Cl(NO_2)$. [136°]. [135°-140°]. Formed from chloro-di-nitro-benzene and phenyl-hydrazine in alcohol (Willgerdt a. Ferko, *J. pr.* [2] 37, 355). Red prisms.

p-Amido-derivative. The compound $NHPh.NH.C_6H_4.NH_2$ [146°] is got by treating $C_6H_5.N_2.C_6H_4.NH_2$ with alcoholic ammonium sulphide (Schultz, *B.* 17, 463). Yellowish plates (from dilute alcohol). Re-oxidised to the *azo*-compound by air.

Di-m-amido-derivative
 $N_2H_4(C_6H_4.NH_2)_2$. [141°] (Gehe, *A.* 251, 193). Got by treatment of *m*-nitro-aniline with alcoholic potash and zinc-dust (Gaeff, *A.* 229, 341), or with sodium-amalgam (Haarhaus, *A.* 135, 164). Golden needles (from alcohol). Yields $C_6H_5.Br.N_2$. [150°] and $C_6H_5.Ac.N_2$. [247°].— $B''H_2Cl_2$.— $B''H_2PtCl_6$.— $B''2HNO_3$.— $B''H_2SO_4$.— $B''H_2C_2O_4$. Prisms, *v.* sl. sol. water.

Di-p-amido-derivative. [145°]. Got by reducing $N_2(C_6H_4.NO_2)_2$ with alcoholic ammonium sulphide (Gerhardt a. Laurent, *A.* 75, 77; Lermontoff, *B.* 5, 232). Yellow crystals. Yields quinone on oxidation.— $B''H_2Cl_2$.— $B''2HNO_3$.

Di-diphenyl-hydrazine v. HYDRAZO-DIPHENYL PHENYL-HYDRAZINE o-CARBOXYLIC ACID $C_6H_5.N_2O$, *i.e.* $NH.NH.C_6H_4.CO_2H$. *Hydrazido-benzoic acid*. Formed from *o*-amido-benzoic acid by diazotising and treating the product with Na_2SO_3 (E. Fischer, *B.* 13, 670; *A.* 212, 333). Needles, sol. hot water. Reduces Fehling's solution in the cold.— $HA'HCl$: needles, sol. hot water.

Anhydride $C_6H_5.N_2O$. [242°]. Formed by heating the acid at 220°. Monoclinic plates (from alcohol); *a:b:c* = 0.772:1:0.64; $\beta = 75^\circ 18'$.

Sublimes in white needles.— $NaO.H.N_2O$ aq: silvery plates.— $B'HCl$: white needles.— $B''HgCl_2$: needles (from water). Yields an acetyl derivative $C_6H_5.Ac.N_2O$ [112°].

Phenyl-hydrazine m-carboxylic acid
 $N_2H_4.C_6H_5.CO_2H$. [186°]. Formed by the action of tin and $HClAq$ on $C_6H_5(CO_2H).N:N.SO_3K$, which is got by warming the nitrate of *m*-diazobenzoic acid with aqueous K_2SO_4 (Griess, *B.* 9, 1657; Roder, *A.* 236, 164). Plates, sl. sol. hot Aq .

Reactions.—1. *Acetone* forms $C_6H_5.H_{12}.N_2O_2$ [150°], which gives EtA' [91°].—2. *Benzoic aldehyde* forms $CHPh:N.NH.C_6H_5.CO_2H$ [172°].—3. *Pyruvic acid* reacts with formation of CO_2 . $CH_3C(=O).N.NH.C_6H_5.CO_2H$ [208°], which forms whetstone-shaped crystals (containing aq), and gives EtA' [104°].—4. *Glucose*, heated with the hydrochloride and $NaOAc$, gives $C_6H_5.H_{12}.N_2O_2$ [208°].—5. *Phenyl-thiocarbimide* forms the compound $C_6H_5.N_2SO_3$ [205°].

Salts.— $HA'HCl$.— BaA'_2 4aq. Nodules.

Phenyl-hydrazine p-carboxylic acid
 $N_2H_4.C_6H_5.CO_2H$. [220°-225°]. Formed, in the same way as its isomerides, from *p*-amido-benzoic acid (Fischer, *A.* 212, 337). Needles or plates (from water).— $HA'HCl$: sl. sol. cold water.

s-Di-phenyl-hydrazine di-o-carboxylic acid
 $C_6H_5.N_2O$, *i.e.* $CO_2H.C_6H_4.NH.NH.C_6H_4.CO_2H$. Mol. w. 272. [205°]. Formed by reducing *o*-azoxy-benzoic acid with sodium-amalgam (Griess, *B.* 7, 1609; Homolka, *B.* 17, 1904). Small colourless plates. Oxidised by moist air to *o*-azobenzoic acid.

s-Di-phenyl-hydrazine di-m-carboxylic acid. Hydrazo-benzoic acid. Formed by boiling *m*-azobenzoic acid with $FeSO_4$ and $NaOH$ (Strecker, *A.* 129, 141). Insol. water, sl. sol. hot alcohol. In alkaline solutions it absorbs O , being oxidised to azobenzoic acid. Boiling conc. $HClAq$ forms azobenzoic acid and amidobenzoic acid. Yields orange-red crystals of BaA' . On warming with $SnCl_2$ and $HClAq$ at 100° it yields di-amido-diphenyl dicarboxylic acid and two other acids. One of these $C_{14}H_{10}.N_2O_4$ crystallises from hot water in yellowish needles and forms BaA'_2 7aq and $HA'HCl$. The other acid $C_{14}H_{12}.N_2O_4$ crystallises in yellow needles melting above 290° and forms NaA' 4aq, BaA'_2 2aq, $HA'HCl$, $HA'HBr$, and $(HA')_2H_2SO_4$ (Kussneroff, *B.* 23, 913).

s-Di-phenyl-hydrazine di-p-carboxylic acid
 $C_6H_5.N_2O$. Formed by boiling *p*-azobenzoic acid with $FeSO_4$ and $NaOH$ (Reichenbach a. Beilstein, *A.* 132, 137; Billfinger, *A.* 135, 152). Needles (from alcohol), easily oxidised in alkaline solution.

s-Di-phenyl-hydrazine tetra-carboxylic acid
 $[1:4:2]C_6H_4(CO_2H)_2.NH.NH.C_6H_4(CO_2H)_2$. [2:1:4]. Formed by reducing azoxyterephthalic acid in alkaline solution with sodium-amalgam (Homolka a. Löw, *B.* 19, 1092). White crystalline pp., *v.* sol. alcohol and ether.

PHENYL-HYDRAZINE m-SULPHONIC ACID $C_6H_5(N_2H_5).SO_3H$. Formed from *m*-amido-benzene sulphonic acid by diazotisation and subsequent reduction by $SnCl_2$ at 0° (Limpricht, *B.* 21, 3409). Crystals (containing 2aq), sl. sol. cold water, nearly insol. alcohol. Converted in alcoholic solution by nitrous acid into $N_2C_6H_5.SO_3H$.

Phenyl-hydrazine p-sulphonic acid
 $[1:4]C_6H_5(N_2H_5).SO_3H$.

Formation.—1. From diazobenzene *p*-sulphonic acid by warming with aqueous K_2SO_3 , followed by HCl (E. Fischer, A. 190, 74).—2. By heating phenyl hydrazine sulphate with $ClSO_3H$ at 160° (Limpricht, B. 18, 2196).—3. Together with alcohol, by heating phenyl-hydrazine ethyl-sulphate at 160° .—4. By heating phenyl-hydrazine (1 pt.) with H_2SO_4 (6 pts.) at 100° (Gallinek a. Richter, B. 18, 3172).

Properties.—Needles (containing $\frac{1}{2}$ aq.), sl. sol. water. By boiling with $CuSO_4$ it is neatly oxidised to N and benzene sulphonic acid. With acetoacetic ether and dilute (50 p. c.) HOAc at 155° it forms $CMe \cdot \begin{smallmatrix} N \\ | \\ N-C_6H_4-SO_2H \\ | \\ CH_3 \cdot CO \end{smallmatrix}$ (Möllenhoff, B. 25, 1849), which crystallises with aq.

Salts.— NaA' , $\frac{1}{2}$ aq.— NH_4A' , $\frac{1}{2}$ aq.— BaA' , $\frac{1}{2}$ aq.— PbA' , $\frac{1}{2}$ aq.— ZnA' , $\frac{1}{2}$ aq.: minute tables.

Phenyl-hydrazine *p*-sulphonic acid. Potassium salt. $C_6H_5NH.NH.SO_3K$. Formed from diazobenzene nitrate and K_2SO_3 (Römer, Z. 1871, 491) and also by heating phenyl-hydrazine with $K_2S_2O_8$ (Fischer, A. 190, 97). Crystals (containing aq.), sl. sol. cold water and alcohol. Oxidised by HgO to $C_6H_5N_2SO_3K$. Split up by boiling $HClAq$ into phenyl-hydrazine and $KHSO_4$.

Phenyl-hydrazine disulphonic acid $NH_2.NH.C_6H_3(SO_3H)_2$. Two acids of this formula are got by further sulphonation of the *m*- and *p*-sulphonic acids respectively (L.). They both yield BaA'' and $BaHA''$.

***s*-Di-phenyl-hydrazine *m*-sulphonic acid** $C_6H_5NH.NH.C_6H_4SO_3H$. Formed by heating the disulphonic acid with water at 200° for 3 days (Limpricht, B. 11, 1048). Yellow needles (containing $\frac{1}{2}$ aq.).— KA' , $\frac{1}{2}$ aq.— PbA' , $\frac{1}{2}$ aq.— BaA' , $\frac{1}{2}$ aq.: yellow plates, v. sol. water.

Chloride $C_6H_5NH.NH.SO_2Cl$. [210°].

Di-bromo-derivative $C_6H_5Br.NH.NH.C_6H_4Br.SO_3H$. Formed as a by-product in the oxidation of $C_6H_5Br.NH.NH.SO_3H$ [1:3:6:4] by $KMnO_4$ (Limpricht, B. 18, 1425).— KA' aq.: long needles.

***s*-Di-phenyl-hydrazine di-*m*-sulphonic acid** $N_2H_2(C_6H_4SO_3H)_2$. S. 079 at 23° . Formed by reduction of nitro-, azo-, or azoxy-benzene-sulphonic acid (Limpricht, B. 11, 1048; 21, 3409; 23, 1057; Bruhnmann, A. 202, 341; Mahrenholz a. Gilbert, A. 202, 337; Neumann, B. 21, 3419). White needles, v. e. sol. water, almost insol. alcohol and ether. Readily reduces ammoniacal $AgNO_3$ and Fehling's solution. $HClAq$ immediately forms benzidine disulphonic acid.— KA'' aq.— BaA'' $\frac{1}{2}$ aq.

Amide $NH(C_6H_4SO_3NH_2).NH.C_6H_4SO_3NH_2$. [248°]. Formed by reducing $N(C_6H_4SO_3NH_2)_2$ with zinc-dust and NH_4Aq or $HOAc$ (Limpricht a. F. Meyer, A. 268, 132). White needles (from 50 p. c. acetic acid), almost insol. water, ether, and toluene. Reduces ammoniacal $AgNO_3$, forming a mirror. $HClAq$ converts it into the amide of diamido-diphenyl (benzidine) disulphonic acid, *m*-amido-benzene sulphonic amide and $N(C_6H_4SO_3NH_2)_2$.— $NH(C_6H_4SO_3NHK)_2$, $\frac{1}{2}$ aq. Thin needles or plates quickly oxidised by air.— $N_2H_2(C_6H_4SO_3NHNa)_2$, $\frac{1}{2}$ aq.: needles.

***s*-Di-phenyl-hydrazine di-*p*-sulphonic acid** $N_2H_2(C_6H_3SO_3H)_2$. Obtained in the same way as the preceding acid, from amido-benzene *p*-sulphonic acid.— $BaHA''$, $\frac{1}{2}$ aq.— BaA'' : crystalline.

Isomeride.—V. BENZIDINE TETRASULPHONIC ACID, vol. I. p. 174.

DI-PHENYL-HYDRAZINE *p*-DI-TRIO-CARBOXYLIC ACID $NPh_2.NH.CS.SH$. [c. 109°]. Formed by dissolving $NPh_2.NH_2$ in CS_2 (Stabel, A. 258, 249). Golden prisms, v. sol. alcohol, insol. water.

***s*-Di-phenyl-hydrazine di-*m*-thiosulphonic acid** $N_2H_2(C_6H_4SO_2SH)_2$. Formed together with $N_2(C_6H_4SO_2SH)_2$ by adding $N_2(C_6H_4SO_2Cl)_2$ to a cold saturated solution of $Ba(SH)_2$ (Limpricht, B. 18, 1470; A. 220, 354). White amorphous pp., becoming sticky on boiling with water. Oxidised by $KMnO_4$ to $N_2(C_6H_4SO_3H)_2$.— BaA'' $\frac{1}{2}$ aq.: minute needles, sl. sol. cold water.

TRI-PHENYL-HYDRAZOIN is Benzhydrazoin, v. *s*-DI-PHENYL-HYDRAZINE, Reaction 5. **DI-PHENYL-HYDROQUINONE** $C_{18}H_{14}O_2$ i.e. $C_6H_5Ph_2(OH)_2$ [5:2:4:1]. [219°]. Formed by reducing di-phenyl-quinone with aqueous SO_2 (Müller a. Feilmann, Z. 23, 2131). Colourless cubes (from dilute alcohol).

PHENYL-IMESATIN v. ISATIN. **PHENYL-IMIDO-DIACETIC ACID** $NPh(CH_2CO_2H)_2$. [150°–155°]. A product of the action of aniline on chloro-acetic acid (P. Meyer, B. 14, 1325; Hausdörfer, B. 22, 1796). Formed also by heating phenyl-amido-acetic acid with chloro-acetic acid and $NaOAc$ at 120° – 130° (H.). Needles, v. sol. hot water and alcohol. $NPhH_2A'$. Needles (from alcohol). Decomposes at 151° .

Mono-anilide $CO_2H.CH_2.NPh.CH_2.CO.NiPh$. [213°]. Formed together with the dianilide by heating the acid with aniline at 175° . Needles. Its ether $CO_2Et.CH_2.NPh.CH_2.CO.NiPh$ [122°] is got by heating the anilide of phenyl-amido-acetic acid (q. v.) with ether and $NaOAc$ at 140° .

Di-anilide $NPh(CH_2CO.NiPh)_2$. [218°]. Needles, v. sl. sol. alcohol.

TRI-PHENYL-TRI-IMIDO-BENZENE $C_6H_5N_3$ i.e. $C_6H_5(NiPh)_3$. [242°]. Formed by warming $C_6H_5Cl_3$ with aniline (Mohr, M. 11, 26). Golden plates, v. sol. chloroform, insol. water and alcohol. Conc. H_2SO_4 gives a dark-blue colour changed to violet by potash.

PHENYL-IMIDO-BENZYL-MALONIC ETHER $C_6H_5C(NPh).CH(CO_2Et)_2$. [75°]. Formed, together with $(C_6H_5C(NPh))_2C(CO_2Et)_2$ by the action of sodium malonic ether on the compound $C_6H_5.CCl.NPh$ (Just, B. 18, 2624). Decomposes at 150° into alcohol and oxy-phenyl-quinoline carboxylic ether.

DI-PHENYL-IMIDO-DI-ETHYL DISULPHONE $NH(CH_2CH_2SO_2C_6H_5)_2$. [78°]. Got by heating $C_6H_5(SO_2C_6H_5)_2$ with NH_4Aq in sealed tubes (Otto, J. pr. [2] 30, 324). Triclinic plates (from alcohol).—Nitrate: [190°].— $BHCl$. [193°].— $B'H_2PtCl_4$: plates, sl. sol. water.

PHENYL-IMIDO-METHENYL-o-AMIDO-PHENOL $C_6H_4 \begin{smallmatrix} NH \\ \diagup \quad \diagdown \\ O \end{smallmatrix} C_6H_4.NPh$. [c. 230°].

Formed by heating $C_6H_4 \begin{smallmatrix} NH \\ \diagup \quad \diagdown \\ O \end{smallmatrix} C_6H_4$ with aniline at 210° (Von Chelmicki, J. pr. [2] 42, 440). Needles, insol. water, sl. sol. cold alcohol.

DI-PHENYL-DI-IMIDO-NAPHTHOL v. (B). **NAPHTHOQUINONE**, Reaction 5.

PHENYL-IMIDO-DINAPHTHYL v. **PHENYL-DINAPHTHYLENE AMINE**.

Compound $C_6H_5O_2(CHPh)_2$ is converted by KOH into $C_6H_5O_2(OH)CH_2Ph$ [185°], and in benzene solution by HNO_3 into $C_6H_5O_2(OH)CH(NO_2)Ph$ [125°] (which yields an acetyl derivative [166°]), and the compound $C_6H_5O_2(NO_2)CH(NO_2)Ph$ [146°], which is converted by boiling alcohol into $C_6H_5O_2C(NO_2)Ph$ [177°], a body that may be reduced by HI and P to iso-benzyl-diphenyl-maleide [118°]. Benzyl-di-phenyl-maleide is converted by alcoholic NH_3 at 180° into $CPh.CH(CH_2Ph) > NH$ [170°], which yields a nitrosamine [136°].

● **PHENYL-MALIC ACID** v. **OXY-PHENYL-SUCINIC ACID**.

● **PHENYL-MALONAMIC ACID** v. **MALONIC ACID**.

● **DI-PHENYL-MALONIC ACID**. *Ethyl ether of the nitrile* $CPh_2(CN)_2CO_2Et$. [59°]. Formed from $CPh_2Cl.CO_2Et$ and $HgCy_2$ at 125° (Bickel, B. 22, 1537). Yellowish tables.

Reference.—**DI-NITRO-PHENYL-MALONIC ETHER**.

● **PHENYL-MANDELIC ACID** v. *Phenyl derivative of* **MANDELIC ACID**.

● **PHENYL-MELAMINE** v. vol. ii. p. 322.

● **PHENYL MERCAPTAN** C_6H_5SH . *Thio-phenol*. *Phenyl-sulphhydrate*. Mol. w. 110. (168°) (L.); (172°) (F. a. C.). S.G. 24 1.078.

Formation.—1. A product of the dry distillation of sodium benzene sulphonate (Kekulé, Z. 1867 194; Stenhouse, A. 149, 248; Pr. 17, 62). 2. Together with Ph_2S and diphenylene sulphide by heating benzene with S and $AlCl_3$ at 75° (Friedel a. Crafts, C. R. 86, 884; A. Ch. [6] 14, 437).—3. By distilling phenol (10 mols.) with P_2S_5 (1 mol.), the yield being 6 p.c. of the phenol used (Kekulé, Z. [2] 3, 193, 306; Beckmann, J. pr. [2] 17, 456).—4. From Ph_2S_2 and K₂S in alcohol (Otto a. Rössing, B. 19, 3129).—5. By distilling $C_6H_5SO_2Na$ with NaSH (Stadler, B. 17, 2080).

Preparation.—Phenyl ethyl dithiocarbonate, or a mixture of diazobenzene chloride solution and potassium ethyl dithiocarbonate (xanthate) is boiled with alcoholic potash until the solution remains clear on addition of water. The alcohol is then distilled off and the residue dissolved in water, mixed with a little H_2SO_4 , and zinc-dust (to prevent oxidation), and distilled with steam. The distillate is extracted with ether. The yield is 75 p.c. of the theoretical (Leuckart, J. pr. [2] 41, 187).

Properties.—Oil, v. sol. alcohol and ether. Smells like garlic. Attacks the skin. Conc. H_2SO_4 forms a violet solution, changing on warming through cherry-red to blue (Baumann, H. 5, 321; cf. Brunner, B. 4, 984).

Reactions.—1. Readily oxidised to Ph_2S_2 .—2. CH_2Cl_2 and dilute (20 p.c.) NaOH aq form $CH_2C(SPh)_2$, crystallising in white plates; v. sol. hot alcohol (Laves, B. 25, 353).—3. *Acetoacetic ether* and dry hydrochloric acid form $CH_2C(SPh)_2.CO_2Et$ [58°], crystallising from alcohol in plates. Not attacked by boiling HCl aq, but decomposed by alkalis into alcohol, $PhSH$, and $CH_2C(SPh):CH.CO_2H$ [177°] (Escales a. Baumann, B. 19, 3790).—4. NH_2COCl forms $NH_2.CO.NH.CO.SPh$ [218°] (Gattermann, A. 244, 43).—5. *Acetone* and HCl in the cold give $Me.C(SPh)_2$ [56°] (Baumann, B. 19, 2804), which is oxidised by $KMnO_4$ and H_2SO_4

to $Me_2C(SO_2Ph)_2$ [97°].—6. *Chloro-acetone* reacts on $PhSNa$ in ether, forming acetonyl-phenyl-sulphide $PhS.CH_2.CO.CH_3$ [35°] (269°) S.G. $\times 1.244$ (Delisle, A. 260, 252). This body crystallises in prisms, sl. sol. hot water, v. sol. alcohol; combines with $KHSO_4$, yields a phenyl-hydrazide [82.5°], and is converted by oxidation into $Ph.SO_2.CH_2.CO.CH_3$ [57°]. Acetonyl-phenyl sulphide may be converted by successive treatment with HCy , alcoholic hydrochloric acid, and alcoholic potash into the acid $PhS.CH_2.CMe(OH).CO_2H$ [97°], which yields CaA' , aq, BaA' , aq, and AgA' , and is oxidised by $KMnO_4$ to $Ph.SO_2.CH_2.CO_2H$ [121°].—7. *Chloral* forms $CCl_3.CH(OH)(SPh)$ [53°], decomposed by heat into its components (Baumann, B. 18, 886).—8. Combines with *pyruvic acid*, forming $CH_2C(OH)(SPh).CO_2H$ [87°], but in presence of gaseous HCl it forms the 'mercaptol' $CH_2C(SPh).CO_2H$ [117°] which is not attacked by boiling HCl aq or alcoholic potash.—9. *Phenyl-glyoxylic acid* forms $C_6H_5C(OH)(SPh).CO_2H$ converted by HCl gas into $C_6H_5C(SPh).CO_2H$ [148°] (Escales a. Baumann, B. 19, 1789).—10. *β -Acetyl-propionic acid* does not combine directly, but in presence of hydrochloric acid it forms $CH_3C(SPh).CH_2.CH_2.CO_2H$ [69°], which is not attacked by alkalis, but is decomposed by dilute acids into $PhSH$ and acetyl-propionic acid (E. a. B.).—11. $CH_3.CO.CH_2SPh$ forms $CH_3C(SPh).CH_2.SPh$ [55°], crystallising in cubes; v. sol. alcohol, insol. water; converted by oxidation in $CH_3C(SPh)(SO_2Ph).CH_2.SO_2Ph$ [157°], crystallising in needles, sl. sol. cold alcohol, split up by alkalis into $PhSO_2.CH_3$, $PhSH$, and $Ph.SO_2H$ (Autenrieth, B. 21, 170).—12. $CBBr_2(SO_2Et)_2$ and $NaOH$ aq form $PhS.CH(SO_2Et)_2$ [86°], crystallising in tables; v. sl. sol. hot water, v. sol. alkalis; converted by alcoholic $NaOH$ and MeI into $PhS.CMe(SO_2Et)_2$ [113°], crystallising in white needles; m. sol. hot alcohol (Fromm, A. 253, 166; Laves, B. 25, 361).—13. $NaSPh$ reacts with isobutylene bromide, forming $NaBr$, PhS_2 , and isobutylene (Otto, B. 23, 1052).

Salts.— $NaSPh$. When Na is dissolved in an ethereal solution of $PhSH$ containing phenol, a pp. of $NaSPh$ is got while $NaOPh$ remains in solution.— $Hg(SPh)_2$: colourless needles (from alcohol).— $CHHgSPh$: plates.— $Pb(SPh)_2$: yellow crystalline pp., split up on distillation into PbS and Ph_2S .— $Cu(SPh)_2$: pale-yellow powder.— $AgSPh$: pale-yellow crystalline pp.

Methyl ether $PhSMe$. (188°). Formed from $Pb(SPh)_2$ and MeI (Obermeyer, B. 20, 2926).

Ethyl ether $PhSEt$. (204°) at 744 mm. Formed from $NaSPh$ and EtI at 120° (Beckmann, J. pr. [2] 17, 457), and by the action of $PhSH$ on PhN_2Cl (Stadler, B. 17, 2078). Liquid with unpleasant smell.

Allyl ether v. **PHENYL ALLYL SULPHIDE**.
Acetyl derivative $PhSac$. (229°). Formed from phenyl mercaptan and $AcCl$ (Michler, A. 176, 177). Oil.

References.—AMIDO-, BROMO-, CHLORO-, CHLORO-NITRO-, NITRO-, and OXY-PHENYL-MERCAPTAN.

● **PHENYL-MERCAPTURIC ACID** $C_6H_4.NSO_2$, i.e. $NHAc.CMe(SPh).CO_2H$. [143°]. Formed by reducing bromo-phenyl-mercapturic acid with

sodium-amalgam (Baumann, *B.* 15, 1732; 18, 258; *H.* 5, 885; 8, 190). Tetrahedra, m. sol. alcohol. Levorotatory in alcoholic solution. Solutions of its salts are dextrorotatory. Decomposed by dilute H_2SO_4 into HOAc and phenylcystein.—BaA', 3aq; needles.

References.—Bromo- and Chloro- Phenyl-Mercapturic Acid.

PHENYL-MESITYL-CARBINOL *v.* PHENYL-TRI-METHYL-PHENYL-CARBINOL.

PHENYL-MESITYL-CARBINOL CARBOXYLIC ANHYDRIDE *v.* TRI-METHYL-PHENYL-PHTHALIDE.

PHENYL MESITYL KETONE *v.* PHENYL-TRI-METHYL-PHENYL KETONE.

PHENYL-METHACRYLIC ACID *v.* PHENYL-CROTONIC ACID.

PHENYL-METHACRYLIC ALDEHYDE $CHPh:CMc.CO.H$. (150° at 100 mm.). Formed by adding NaOHaq to a mixture of benzoic aldehyde and propionic aldehyde (Miller a. Kinkel, *B.* 19, 525). Oil. Reduces ammonia $AgNO_3$. Combines with bisulphite. Yields a phenyl-hydrazide [137°].

PHENYL-METHANE *v.* TOLUENE. $Di-phenyl-methane C_6H_5.C_6H_5$, i.e. CH_2Ph_2 . Mol. w. 168. [25°]. (c. 263°).

Formation.—1. Together with $C_6H_5(CH_2Ph)_2$, by boiling benzyl chloride with benzene and zinc-dust (Zincke, *B.* 4, 298; *C. J.* 24, 508, 688). 2. By the action of H_2SO_4 and HOAc on a mixture of benzene and benzyl alcohol (Meyer a. Wurster, *B.* 6, 963).—3. By heating benzophenone with zinc-dust (Staedel, *B.* 6, 1401; 7, 1480; *cf.* Barbier, *C. R.* 79, 812), or by reducing it with HI and P (Graebe, *B.* 7, 1624), or Zn and H_2SO_4 (Zincke, *B.* 10, 1473).—4. From benzene, CH_2Cl_2 , and $AlCl_3$ (Friedel a. Crafts, *Bl.* [2] 41, 824; *A. Ch.* [6] 11, 264).—5. From $CH_3(OMe)_2$, benzene, HOAc, and H_2SO_4 (Baeyer, *B.* 6, 221).—6. By distilling barium di-phenylacetate with soda-lime (Jena, *A.* 155, 86).

Preparation.—By adding $AlCl_3$ (35 g.) to a mixture of benzyl chloride (100 g.) and benzene (500 g.) (Friedel a. Crafts, *A. Ch.* [6] 1, 478; *Bl.* [2] 33, 337).

Properties.—Prisms, v. sol. alcohol and ether, smelling like oranges. According to Reissert (*B.* 23, 2242) it melts at 28°. Oxidised by chromic acid mixture to benzophenone. Yields diphenylene-methane when passed through a red-hot tube (Graebe, *B.* 7, 1623). Prolonged treatment with Cl in presence of I forms CCl_4 and C_2Cl_4 (Ruoff, *B.* 9, 1048).

Tri-phenyl-methane $C_6H_5_3$, i.e. $CHPh_3$. [92°]. (330°) (Schwarz); (355°) (K. a. F.).

Formation.—1. By heating $PhCHCl_2$ with $HgPh_2$ at 150° (Kekulé a. Franchimont, *B.* 5, 907).—2. By heating $Ph.CH(OH)$ with benzene and P_2O_5 at 135° (Hemilian, *B.* 7, 1203).—3. By heating (8) benzpinacolin $C_{10}H_{12}O$ with soda-lime at 300° (Thörner a. Zincke, *B.* 9, 65).—4. Together with a little CH_2Ph_2 , by adding $AlCl_3$ to a mixture of chloroform and benzene (Friedel a. Crafts, *J. pr.* [2] 16, 233; *A. Ch.* [6] 1, 496). 5. With other products, by the action of $AlCl_3$ on benzene mixed with CH_2Cl_2 , with CCl_4 , with $PhCCl_3$, and with $CPHBr.CPhHBr$ (Magatti, *B.* 12, 1408; Schwarz, *B.* 14, 1526; Anschütz, *A.* 235, 208).—6. By heating benzoic aldehyde

(100 g.) with benzene (147 g.) and $ZnCl_2$ (100 g.) at 280° for 7 hours (Griepentrog, *B.* 19, 1876; *A.* 242, 329).

Preparation.— $AlCl_3$ (500 g.) is slowly added to a mixture of benzene (1400 g.) and chloroform (400 g.). The mixture is finally heated on the water-bath, water is carefully added, and the oil dried and fractionally distilled. It is finally purified by conversion into the compound with benzene (Allen a. Kölliker, *Z.* 227, 108; *cf.* Fischer, *A.* 194, 252; Schwarz, *B.* 14, 1516). If the benzene contains toluene the product will contain a homologue (Hanriot, *Bl.* [3] 1, 773).

Properties.—Plates (from alcohol), v. sol. benzene, ether, and $CHCl_3$, m. sol. cold alcohol. Crystallises from benzene in efflorescent rhombohedra $CHPh_3.C_6H_5$ [76°]. Oxidised by chromic acid to tri-phenyl-carbinol [159°]. $AlCl_3$ at 120° decomposes it, but below 80° it forms CH_2Ph_2 (Friedel a. Crafts, *C. R.* 100, 692). On exhaustive chlorination with $SbCl_5$ it yields CCl_4 and C_2Cl_4 (Merz a. Weith, *B.* 16, 2876). Na has no action at 300°, but K at 200° forms a red substance ($CKPh_3$). K at 250° forms a dark mass, whence $HClAq$ liberates C_6H_5 , [148-5°] (360°) (Hanriot a. Saint-Pierre, *C. R.* 108, 1119; *Bl.* [3] 1, 774). The potassium derivative $CKPh_3$ absorbs CO_2 at 200°, yielding $CPH.CO_2H$ [264°]. Benzyl chloride acting on $CKPh_3$ forms the compound $CPH_2.CH_2Ph$ [140°]. $BzCl$ forms $C_{10}H_8O$ [172°] which may be reduced by HI and P to $C_{10}H_8$ [234°].

References.—AMIDO-, BROMO-, CHLORO-, METHYL-AMIDO-, NITRO-, NITRO-AMIDO-, OXY-AMIDO-, and OXY- PHENYL-METHANE.

DI-PHENYL-METHANE DI-O-CARBOXYLIC ACID $CH_2(C_6H_4.CO_2H)_2$. [255°]. Formed by reducing the lactone of $CH(OH)(C_6H_4.CO_2H)_2$ with HI and P (Graebe a. Juillard, *A.* 242, 253). Crystals (from alcohol). Yields anthraquinone on heating at 280°.—BaA' 6aq. *S.* 4.7.

Methyl ether $Me.A'$. [44°].

Isomeride v. BENZYL-ISOPHTHALIC ACID.

Di-phenyl-methane tricarboxylic acid $CO_2H.CH(C_6H_4.CO_2H)_2$. [220°]. *S.* -095 at 25°. Got by heating the lactone of the oxyacid $CO_2H.C(OH)(C_6H_4.CO_2H)_2$ with HI and P at 170° (Graebe a. Juillard, *A.* 242, 235). Crystals (containing aq.). At 270° it forms a red compound $C_{10}H_8O_4$ [261°].

Methyl ether $Me.A'''$. [145°].

Tri-phenyl methane o-carboxylic acid $CHPh_2.C_6H_4.CO_2H$. [162°].

Formation.—1. By the action of NaOH an zinc-dust on di-phenyl-phthalide (Baeyer, *B.* 15, 644; *A.* 202, 52).—2. By heating phenyl phthalide with benzene and $AlCl_3$ (Gresly, *A.* 234, 242).—3. By saponifying the nitrile, which is obtained from $CHCl_2.C_6H_4.CN$, benzene, and $AlCl_3$ (Drory, *B.* 24, 2572).

Properties.—Needles (from alcohol), insol. water. May be sublimed. Yields tri-phenyl methane when heated with $Ba(OH)_2$. CrO_3 in HOAc oxidises it to diphenyl-phthalide.

Nitrile $CHPh_2.C_6H_4.CN$. [69°].

Tri-phenyl methane p-carboxylic acid [162°]. Obtained by saponifying the nitrile which is obtained by Sandmeyer's reaction from p-amido-tri-phenyl-methane [84°] (Fischer a. Fränkel, *A.* 241, 364; Otto a. Fischer, *B.* 24, 729). Needles, v. sol. alcohol and ether.—A₂A₂'.

An isomeric acid melting above 360° was obtained by Oppenheimer (*B. 19, 3029*) by oxidising the corresponding aldehyde with Ag_2O .

Tri-phenyl-methane dicarboxylic acid
 $\text{CHPh}_3\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ [1:2:5]. [280°]. Formed by reduction of the lactone of tri-phenyl-carbinol dicarboxylic acid by zinc-dust and NaOH (Hemilian, *B. 16, 2375*). Needles (from HOAc). Conc. H_2SO_4 forms a greenish-yellow solution, which on heating changes through green, blue, and violet to purple.— BaA'' 4aq.— $\text{Ag}_2\text{A}''$: pp. *

Tri-phenyl-methane dicarboxylic acid
 $\text{CHPh}_3\text{C}_6\text{H}_4(\text{CO}_2\text{H})_2$ [1:3:4]. [78°]. Formed by boiling di-phenyl-phthalide dicarboxylic acid with zinc-dust and NaOHAq (Hemilian, *B. 19, 3068*). Needles (from dilute alcohol). May be sublimed. Yields CHPh , when distilled with Ba(OH)_2 . Re-oxidised by alkaline KMnO_4 to di-phenyl-phthalide dicarboxylic acid.— CaA'' 2aq: needles.— $\text{Ag}_2\text{A}''$: curdy pp.

Reference.—OXY-DI-PHENYL-METHANE CARBOXYLIC ACID.

DIPHENYL-METHANE DISULFONIC ACID $\text{C}_{12}\text{H}_{10}(\text{SO}_3\text{H})_2$ [59°]. Got by sulphonation (Doer, *B. 5, 796*). Deliquescent plates.— KA'' aq: prisms (from dilute alcohol).— BaA'' .— CuA'' : green plates.

Tri-phenyl-methane trisulphonic acid
 $\text{C}_{12}\text{H}_9(\text{SO}_3\text{H})_3$. Formed by warming CHPh with fuming H_2SO_4 (Kekulé & Franchimont, *B. 5, 908*; Hemilian, *B. 7, 1205*).— $\text{Ba}_2\text{A}'''$ 8aq: needles, ppd. by adding alcohol to its aqueous solution.

DI-PHENYL-METHAZINE $\text{C}_{11}\text{H}_{12}\text{O}_2$, i.e. $\text{CHPh} \begin{smallmatrix} \text{N} \\ \diagup \quad \diagdown \\ \text{C} \end{smallmatrix} \text{CHPh}$. [93°]. Formed by shaking a dilute solution of hydrazine with benzoic aldehyde (Curtius, *J. pr.* [2] 39, 44). Light-yellow prisms, v. sl. sol. hot water, v. sol. hot alcohol. Decomposed by boiling into CHPh and CHPh and nitrogen, and by boiling dilute acids into benzoic aldehyde and hydrazine. Reduced in alcoholic solution by sodium-amalgam to di-benzyl-hydrazine, and by excess of Na to benzylamine.

PHENYL-METHENYL-AMIDINE v. BENZAMIDINE.

Diphenyl-methenyl-diamine is described as DI-PHENYL-FORMAMIDINE.

PHENYL-METHENYL-AZIDINE $\text{C}_{11}\text{H}_9\text{N}_3$, i.e. $\text{NH}_2\text{CH}:\text{N}:\text{NPh}$. [225°]. Formed from phenylhydrazine and HCy (Fischer, *B. 22, 1934*). Insol. water, v. sol. hot alcohol. The nitrate and hydrochloride are crystalline.

PHENYL METHENYL DI-ETHYL TRISULPHONE $\text{C}_{12}\text{H}_{14}\text{SO}_4\text{CH}(\text{SO}_2\text{C}_2\text{H}_5)_2$. [166°]. S. 2 at 15°. Formed by oxidising $\text{PhS.CH}(\text{SO}_2\text{Et})_2$ with alkaline KMnO_4 (Fromm, *A. 253, 167*; Laves, *B. 25, 362*). Snow-white needles, v. sol. alkalis.— KA' : prisms.— BaA'_2 : tables.

TRI-PHENYL-METHENYL TRIKETONE v. TRI-BENZOYL-METHANE.

TRI-PHENYL-METHENYL TRISULPHONE $\text{CH}(\text{SO}_3\text{Ph})_3$. [215°]. Formed by oxidising $\text{PhS.CH}(\text{SO}_3\text{Ph})_2$ with alkaline KMnO_4 (Laves, *B. 25, 348*). Tables, v. sol. alcohol, insol. ether, m. sol. water.— KA' : tablets.— BaA'_2 .— AgA' .

DI-PHENYL-DI-METHYL ACETYLENE TETRAKETONE v. DI-BENZOYL-DI-ACETYLENE.

PHENYL-METHYL-ACRIDINE $\text{C}_{14}\text{H}_{11}\text{N}$, i.e.

$\text{C}_6\text{H}_5 \begin{smallmatrix} \text{CPh} \cdot \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CMe} \\ \text{N} \quad \text{C}_6\text{H}_4 \cdot \text{CH} \cdot \text{CMe} \end{smallmatrix}$ [186°]. Formed by heating phenyl-*p*-toluidine with benzoic acid and ZnCl_2 at 260° (Bonna, *A. 289, 62*). Needles, sl. sol. water. Its alcoholic solution shows greenish-blue fluorescence. Yields phenyl-acridine carboxylic acid [253°] on oxidation.— B'HI : yellow needles.— B'HI .— $\text{B'H}_2\text{SO}_4$.— $\text{B'C}_2\text{H}_5\text{N}_3\text{O}_2$. Red needles.

Phenyl-methyl-acridine dihydride.

$\text{C}_6\text{H}_5 \begin{smallmatrix} \text{CHPh} \\ \text{NMe} \end{smallmatrix} \text{C}_6\text{H}_4$ [104°]. Formed by the action of MeI on phenyl-acridine dihydride; or by reduction of the methylo-chloride of phenyl-acridine with zinc-dust (Berthsen & Bender, *B. 16, 1816*). White needles or prisms. On oxidation with nitrous acid it gives the methylo-hydroxide of phenyl-acridine.

PHENYL-METHYL-ALLYL-PYRROLE

$\text{CH}:\text{CMe} > \text{NC}_6\text{H}_5$. [52°]. [278°]. Formed by heating the carboxylic acid [158°] (Lederer & Paal, *B. 18, 2595*). Large colourless plates. Blue fluorescence. Extremely sol. all ordinary solvents.

PHENYL-METHYL-ALLYL-PYRROLE

CARBOXYLIC ACID $\text{CH}:\text{CPh} > \text{NC}_6\text{H}_5$. [158°]. Obtained by saponification of its ether, which is formed by the action of allylamine upon acetophenone-acetoacetic ether (Lederer & Paal, *B. 18, 2594*). Short glistening prisms. V. sol. alcohol, ether, benzene, and acetic acid.

PHENYL-METHYL-AMIDO-ACETIC ACID $\text{C}_{12}\text{H}_{11}\text{NO}_3$, i.e. $\text{CH}_2(\text{NPhMe})\text{CO}_2\text{H}$. *Phenyl-methyl-glycocol*. Formed by heating chloro-acetic ether with dimethylaniline and saponifying the product by boiling HClAq (Silberstein, *B. 17, 2661*). Liquid.— HA'HCl : prisms.

Amide. $\text{CH}_2(\text{NPhMe})\text{CO}_2\text{NH}_2$. [168°]. Formed by heating $\text{CH}_2\text{ClCONH}_2$ with NPhMe_2 or NPhMeI . Crystals, sol. hot water. Its hydrochloride forms easily soluble prisms.

Methylo-chloride $\text{CH}_2(\text{NPhMeCl})\text{CO}_2\text{H}$. Formed by warming chloro-acetic acid with NPhMe_2 in ether (Zimmermann, *B. 12, 2206*). Needles. Moist Ag_2O forms an hydroxide.

Amide of the methylo-chloride
 $\text{CH}_2(\text{NPhMeCl})\text{CO}_2\text{NH}_2$. Formed by heating chloro-acetamide with dimethylaniline in alcohol (S.). Crystals, decomposed by heat into MeCl and $\text{CH}_2(\text{NPhMe})\text{CO}_2\text{NH}_2$.

PHENYL-METHYL- ω -AMIDO-ACETO-PHENONE $\text{C}_{14}\text{H}_{13}\text{CO}_2\text{CH}_2\text{NPhMe}$. *Phenacyl-methyl-aniline*. [120°]. Formed by the action of NPhMeI or NPhMe on ω -bromo-acetophenone (Staedel & Siepermann, *B. 18, 842*; 14, 983; 21, 2196). Prisms (from alcohol). A solution of its hydrochloride gives a red pp. with dilute HNO_3 (Weller, *B. 16, 27*). ZnCl_2 forms $\text{C}_{14}\text{H}_{11}\text{N}$ [102°].— $\text{B'H}_2\text{PtCl}_4$: tables.— B'MeI . Crystals.— B'MeOH . Strongly alkaline.

PHENYL-METHYL-AMIDO-BENZENE PHOSPHINIC ACID $\text{NPhMe.C}_6\text{H}_4\text{P(OH)}_2$ [150-5°]. Formed by the action of NaOHAq on the oily chloride $\text{NPhMe.C}_6\text{H}_4\text{PCL}_2$, which is formed by the action of AlCl_3 on a mixture of NPh_2Me and PCl_3 (Michaelis, *A. 260, 87*). Small needles (from water) or plates (from alcohol).— NaHA'' 2aq. [265°]. Plates, v. e. sol. water.

PHENYL-METHYL-AMIDO-BENZOIC ACID $C_{11}H_9NO_2$, i.e. $C_6H_5(NPhMe).CO_2H$. [184°]. Formed from $NPhMe$ and $COCl_2$ (Michler a. Sarauw, B. 14, 2180). Plates.—BaA': pearly plates.—AgA': white pp.

PHENYL-METHYL-AMIDO-ETHANE SULPHONIC ACID $NPhMe.C_2H_5.SO_3H$. Formed from $CH_3Cl.C_2H_5.SO_3H$ and methylaniline at 160° (James, J. pr. [2] 31, 417). Silky crystals (from alcohol).

PHENYL-METHYL-AMIDO-ETHYL-PHTHALIMIDE $C_{14}H_{11}O_2.N.C_6H_5.NPhMe$. [105°]. Formed from bromo-ethyl-phthalimide and methyl-aniline at 165° (Newman, B. 24, 2199). Greenish-yellow four-sided tables, a c. sol. C_6H_6 .

PHENYL-METHYL-AMIDO-METHENYL-AMIDO-PHENOL $C_{11}H_9N_2O$. i.e.

$C_6H_5 \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N \\ N \end{smallmatrix} C.NPhMe$. (above 360°). Formed from $C_6H_5 \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} N \\ N \end{smallmatrix} C.SH$ and • methyl-aniline (Kalkhoff, B. 16, 1825). • Syrup, with blue fluorescence.—B'H₂PtCl₄: prisms.

PHENYL-METHYL-AMIDO-DI-METHYL-PYRROLE $C_{11}H_9N_2$, i.e. $NPhMe.N \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CH \\ CH \end{smallmatrix} CMe$. [41°]. (310°). Formed by heating its dicarboxylic acid at 231° (Knorr, A. 236, 310). Crystalline mass, v. sol. alcohol. Volatile with steam.

Phenyl-methyl-amido-di-methyl-pyrrole dicarboxylic acid $C_{11}H_9N_2O_4$. Formed by saponification of its oily ether, which is formed from diacetyl-succinic ether and phenyl-methyl-hydrazine (K.). Prisms, decomposing at 231°.—AgA': flocculent pp.

PHENYL-METHYL-p-AMIDO-PHENOL. Methyl derivative $NPhMe.C_6H_4.OMe$. (313°). Formed from phenyl-p-amido-phenol, KOH, and MeI (Philip a. Calm, B. 17, 2433). Oil, insol. NaOHaq.

PHENYL-TETRA-METHYL-TRI-AMIDO-DI-PHENYL-NAPHTHYL-CARBINOL $C_{22}H_{15}N_3O$, i.e. $NPhH.C_6H_4.C(OH)(C_6H_5.NMe_2)_2$. [95°]. Base of Victoria Blue B. Formed by heating tetra-methyl-di-amido-benzophenone (10 pts.) with phenyl-(a)-naphthylamine (9 pts.), and POCl₃ (7 pts.) at 110° (Nathansohn a. Müller, B. 22, 1890). The base is set free by NaOHaq. Brick-red powder, v. sol. alcohol and benzene.— $(C_6H_5N_2Cl)_2.PtCl_4$: violet needles.— $C_6H_5N_3.C_6H_4(NO_2)_2.OH$: dark-blue pp.

Phenyl-penta-methyl-tri-amido-di-phenyl-naphthyl-carbinol $C_{23}H_{17}N_3O$, i.e. $NPhMe.C_6H_4.C(OH)(C_6H_5.NMe_2)_2$. [77°]. The chloride $C_{23}H_{17}N_3Cl$, 'Victoria Blue 4 R', formed by the action of methyl-phenyl-(a)-naphthylamine on $CO(C_6H_5.NMe_2)_2$ in presence of POCl₃ is v. sol. hot water (Nathansohn a. Müller, B. 22, 1892). The carbinol is a brick-red pp., v. sol. alcohol. It forms $(C_{23}H_{17}N_3Cl)_2.PtCl_4$ and $C_{23}H_{17}N_3.C_6H_4(NO_2)_2.OH$ crystallising in very small dark-blue needles.

PHENYL-TETRA-METHYL-TRI-AMIDO-DI-PHENYL-NAPHTHYL-METHANE $C_{22}H_{15}N_3$, i.e. $NPhH.C_6H_4.CH(C_6H_5.NMe_2)_2$. [125°]. Formed by reducing the carbinol (v. supra) (Nathansohn a. Müller, B. 22, 1891). Flocculent pp., v. sol. hot alcohol. Yields B''H₂PtCl₄ and B'''C₆H₄N₃O, both being crystalline.

Phenyl-penta-methyl-tri-amido-di-phenyl-naphthyl-methane $C_{23}H_{17}N_3$, i.e.

$NPhMe.C_6H_4.CH(C_6H_5.NMe_2)_2$. [87°]. Formed by reducing the carbinol (N.a.M.). Amorphous. Yields crystalline B'''H₂PtCl₄ and B'''C₆H₄N₃O.

PHENYL-DI-METHYL-AMIDO-TOLYL KETONE $C_9H_7.CO.C_6H_5.Me.NMe_2$. [67°]. (350°-360°). Formed from benzoic acid, di-methyl-toluidine, and P₂O₅ (O. Fischer, A. 206, 91).

PHENYL-TETRA-METHYL-DI-AMIDO-DI-TOLYL-METHANE $C_{22}H_{15}N_2$, i.e.

$CHPh(C_6H_5.Me.NMe_2)_2$. [109°]. Formed by heating di-methyl-m-toluidine with benzoic aldehyde and ZnCl₂ (Fischer, B. 13, 807). Prisms.—B'H₂PtCl₄ 2aq: small yellow crystals.

PHENYL-METHYL-AMINE v. METHYL-ANILINE.

Phenyl-di-methyl-amine v. DI-METHYL-ANILINE.

Di-phenyl-methyl-amine v. • METHYL-DI-PHENYL-AMINE.

Tri-phenyl-methyl-amine v. TRI-PHENYL-CARBINYLAMINE.

PHENYL-METHYL-ANTHRACENE $C_{21}H_{16}$, i.e. $C_6H_5.Me \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CPh \\ CPh \end{smallmatrix} > C_6H_4$. [119°]. Obtained by distilling phenyl-methyl-anthranol with zinc dust (Hemilian, B. 16, 2367). Yellow pointed crystals. Dissolves in alcohol and ether, with a strong greenish-blue fluorescence. By CrO₃ in acetic acid it is oxidised to phenyl-methyl-oxanthranol.

PHENYL-METHYL-ANTHRANOL $C_{21}H_{16}O$, i.e. $C_6H_5.Me \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CPh \\ C(OH) \end{smallmatrix} > C_6H_4$. [157°]. Obtained by heating di-phenyl-tolyl-methane carboxylic acid with H₂SO₄ (Hemilian, B. 16, 2365). Yellow glistening tables. Sol. ether, boiling alcohol and acetic acid, insol. cold alkalis, but dissolves on boiling to a yellow solution. On oxidation it gives phenyl-methyl-oxanthranol.

PHENYL-DI-METHYL-ARSINE v. vol. i. p. 320.

DI-PHENYL-DI-METHYL-AZIMETHYLENE $N_2(CMePh)_2$. [1212]. Formed by the action of acetophenone on hydrazine hydrate or on $CPhMe.N.NH_2$ (Curtius, J. pr. [2] 44, 542).

PHENYL-METHYL-BIAZOLE DIHYDRIDE $O \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CH_2.NPh \\ CMe.N \end{smallmatrix}$. [140°]. Formed by the action of tin and HCl on $O \begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} CCl_2.NPh \\ CMe.N \end{smallmatrix}$ [122°], which is made by the action of COCl₂ on acetyl-phenyl-hydrazine (Freund a. Kuh, B. 23, 2838). Yellowish plates.

PHENYL-METHYL-TRIAZOLE $C_8H_7N_3$, i.e. $N.NPh > CH$. Formed by heating its carboxylic acid to 180° (Bladin, B. 19, 2602). Oil, B'H₂PtCl₄ aq. [124°]. Lemon-yellow tables.

PHENYL-METHYL-TRIAZOLE CARBOXYLIC ACID $N.NPh > C.CO_2H$. [177°]. Formed by saponifying its nitrile, which is got by the action of Ac₂O on phenyl-hydrazine dicyanide and also by gently warming phenyl-hydrazine dicyanide with an alcoholic solution of pyruvic acid (Bladin, B. 18, 1544; 19, 2598; 22, 1749; 25, 185).

Salts. — CuA', 11aq. — PbA', 21aq. — AgA' 11aq. — HA'HCl: tables (from HCl aq.).

PHENYL-THIO-SEMICARBAZIDE $C_6H_5N_3S$ i.e. $NH_2CS.NH.NHPh$. [201° (F.; P.); [190° (S. a. R.).

Formation.—1. By warming di-phenyl-thiocarbazine with alcoholic or aqueous alkalis (Fischer, A. 212, 324).—2. By heating phenylhyd

TITANOTUNGSTIC ACIDS. Two acids, $(\text{H}_2\text{O} \cdot \text{TiO}_2 \cdot 12\text{WO}_3 \cdot x\text{H}_2\text{O})$ and $(\text{H}_2\text{O} \cdot \text{C}_2\text{TiO}_2 \cdot 10\text{WO}_3 \cdot x\text{H}_2\text{O})$, are described by Lejarme (v. Klein, *Bl.* [2] 36, 17).

VANADOTUNGSTIC ACIDS AND SALTS. Several compounds of WO_3 with V_2O_5 and H_2O have been described by Gibbs (*Ann.* 4, 377; 5, 361, 391) and Rosenheim (*A.* 251, 197); they belong to the forms $\text{V}_2\text{O}_5 \cdot 10\text{WO}_3 \cdot x\text{H}_2\text{O}$, $\text{V}_2\text{O}_5 \cdot 18\text{WO}_3 \cdot x\text{H}_2\text{O}$, and $\text{V}_2\text{O}_5 \cdot 4\text{WO}_3 \cdot x\text{H}_2\text{O}$. Compounds of these with $\gamma\text{M}_2\text{O}$ and γMO are also described; and a great variety of compounds coming under the general formula $x\text{MO} \cdot y\text{V}_2\text{O}_5 \cdot z\text{WO}_3 \cdot w\text{H}_2\text{O}$ have been obtained (cf. Friedheim, *B.* 23, 1505; and Rothenbach, *B.* 23, 3050).

Tungsten, oxybromides of. Two oxybromides, WO_2Br_2 and WOBr_4 , are formed by the reaction of Br on WO_3 and in other ways. The formula WOBr_4 is very probably molecular, from the analogy of WOCl_4 .

Tungsten dioxidebromide WO_2Br_2 . Obtained by heating WO_3 in a stream of Br vapour, also by passing vapour of WBr_3 over heated VO_3 (Roscoe, *C. N.* 25, 73); also by heating VS_2 or a mixture of WO_3 and C in Br (Borck, *J.* pr. 54, 254). Red, transparent, prismatic crystals; appearing black when hot, and giving a yellow powder. Volatilised at red heat with partial decomposition to WO_3 and WOBr_4 .

Tungsten oxytetrafluoride WOBr_4 . Obtained by passing Br vapour over a heated mixture of equal parts of WO_3 and W, and autously distilling from less volatile WO_2Br_2 (Roscoe, *C. N.* 25, 73). Also formed by passing Br mixed with some Overheated W, or by heating a mixture of WO_3 and C in Br vapour (Blomstrand, *J.* pr. 82, 430). Brownish black, lustrous, crystalline needles; melts at 277° and boils at 27° . Heated in moist air gives WO_3 and HBr , and is decomposed to the same products by water.

Tungsten, oxychlorides of. Two oxychlorides, WO_2Cl_2 and WOCl_4 , are formed by heating W in Cl mixed with some O, and in other reactions.

Tungsten dioxidechloride WO_2Cl_2 . Obtained by heating WO_3 in a stream of Cl, and subliming (Roscoe, *C. N.* 25, 63); also by passing CO_2 over a mixture of WO_3 and CaCl_2 heated to redness (Schultze, *J.* pr. [2] 21, 432). Also formed, along with WOCl_4 , by heating W in Cl mixed with O; by heating WO_3 and C in Cl; by heating WO_3 in CCl_4 (Watts a. Bell, *C. J.* 33, 42); and by heating WO_3 with PCl_5 (Schiff, *M.* 97, 185; cf. Tungsten trioxide, *Reactions*, *loc.* 10, p. 801). Yellow, four-sided tablets; sublimes without melting at $c. 266^\circ$, with partial decomposition to WO_3 and WOCl_4 . Not decomposed in moist air, nor by cold water (R., *L.c.*). Heated in dry NH_3 gives off NH_4Cl and leaves VO_2 (Rideal, *C. J.* 55, 48); in this reaction VO_2Cl_2 behaves like CrO_2Cl_2 (R., *C. J.* 49, 367); according to Smith a. Shinn (*Zeit. f. anorg. Chemie*, 4, 381), a black compound $\text{W}_2\text{O}_7\text{N}_2\text{H}_2$ is formed by heating WO_2Cl_2 in dry NH_3 .

Tungsten oxytetrafluoride WOCl_4 . Mol. r. 341.04. Formed by heating W in Cl containing a little O; also by passing Cl over a hot mixture of WO_3 and C; by heating WO_3 in CCl_4 (Watts a. Bell, *C. J.* 33, 442); by heating VOCl_3 or WCl_5 in O and Cl; by heating WCl_5 with

$\text{H}_2\text{C}_2\text{O}_4$; and by heating WO_2Cl_2 . Prepared by passing vapour of WCl_5 over heated WO_3 in a current of Cl (Roscoe, *C. N.* 25, 63). Also by heating WO_3 and PCl_5 in the ratio $\text{WO}_3 \cdot \text{PCl}_5$ or $\text{WO}_3 \cdot 2\text{PCl}_5$, distilling off POCl_3 , and the small quantities of WCl_5 and WCl_4 that are formed, washing the reddish residue with a little cold CS_2 (to remove WCl_5), then dissolving in a larger quantity of warm CS_2 , evaporating, and carefully heating the residue in a stream of CO_2 , whereby the more volatile WOCl_4 is separated from WO_2Cl_2 (Schiff, *A.* 197, 185).

WOCl_4 forms ruby-red, transparent needles; melts at 210.4° , and volatilises at 227.5° , forming a yellow vapour (R., *L.c.*). V.D. 170.2 to 175.8 at 350° , 171.5 at 440° (R., *L.c.*; cf. Debray, *C. R.* 60, 820). Exposure to air produces a crust of yellow WO_2Cl_2 . Heated in NH_3 probably gives W_2N_2 (Rideal, *C. J.* 65, 43). Decomposed by water, with a hissing sound, to WO_3 and HCl (Roscoe, *L.c.*).

Tungsten, oxyfluorides of. No compound of W with O and F has been isolated, but compounds are known which may be regarded as containing WO_2F_2 . These compounds, $\text{WO}_2\text{F}_2 \cdot 2\text{MF}$ and $\text{WO}_2\text{F}_2 \cdot \text{MF}$, and also a compound $\text{WO}_2\text{F}_2 \cdot 2\text{KF}$, are described under Tungsten oxyfluorides (p. 799).

Tungsten, phosphides of. By heating W in vapour of P, a dark-grey powder was obtained by Wöhler a. Wright (*A.* 79, 244), to which they gave the composition W_2P_3 . By heating a mixture of WO_3 and P_2O_5 in a graphite crucible, W. a. W. (*L.c.*) obtained large, dark-grey, lustrous, six-sided prisms; S.G. 5.207; insoluble in acids, including *aqua regia*, soluble in a molten mixture of Na_2CO_3 and NaNO_3 ; unchanged by heating in air, but burns brilliantly in O. From an estimation of the P, W. a. W. gave the formula W_2P_3 .

Tungsten, salts of. No salts have been isolated by replacing the H of oxyacids by W. Except the halides, the only salts of W that are known are those wherein W forms part of the negative radicle.

Tungsten, selenides of. By saturating a solution of $\text{Na}_2\text{W}_2\text{O}_7$ with H_2Se , and then adding dilute H_2SO_4 , Ueismann (*A.* 116, 125) obtained a black pp., to which he gave the formula WSe_2 (the estimation of W is given); by heating this in a tube a grey solid was obtained, said by U. to be WSe_2 (no analyses). WSe_2 is said to be easily soluble in solutions of alkalis, alkali sulphides, or alkali selenides.

Tungsten, sulphides of. Two compounds of W and S are known, WS and WS_2 ; the latter is acidic, forming salts MWS_2 . The V.D. of neither has been determined.

Tungsten disulphide WS_2 . Obtained by heating WO_3 to whiteness in vapour of S or in H_2S (Berzelius); also by heating W and S; also by heating WO_3 with 6 pts. HgS out of contact with air (Borck, *J.* pr. 54, 254). According to Carnot (*Bl.* [2] 32, 164), WS_2 is usually formed when a compound of W is heated in a stream of dry H_2S (v. also von Usler, *A.* 94, 256; Combes, *A.* 232, 262). A dark-grey, graphite-like, lustrous, crystalline powder (v. Riche, *M. Ch.* [3] 50, 26). Is said to decompose steam at a full red heat; reduced to W by very long continued heating in H.

TUNGSTEN TRISULPHIDE WS_3 . Obtained by fusing powdered wolframite with 2 pts. C, 3 pts. S, and 3 pts. Na_2CO_3 , dissolving in water, decomposing the Na_2WS_4 thus produced by $HClAq$, washing the pp. completely out of contact with O, and drying at 100° (von Usler, A. 94, 256; Corleis, A. 232, 264). A black powder; slightly soluble in water, more soluble on boiling, probably with partial decomposition. Soluble in alkali sulphide solutions, forming thio-salts (v. Tungsten, thio-acids and salts of, *infra*). By adding to Na_2WS_4 a little more $HClAq$ than was needed to combine with the Na, Winsinger (Bt. [2] 49, 452) obtained a colloidal form of WS_3 .

Tungsten, sulpho-acids and salts of, v. next article.

Tungsten, thio-acids and salts of. By saturating $(NH_4)_2WO_4$ and K_2WO_4 with H_2S , Berzelius obtained $(NH_4)_2WS_4$ and K_2WS_4 (P. 8, 267); these salts were more fully examined by Corleis (A. 232, 258), who also obtained Na_2WS_4 , and also some thio-oxy-tungstates. All the thio-tungstates that have been isolated are ortho-salts, i.e. salts of H_2WS_4 . Very dilute solutions of thiotungstates can be titrated with IAq in presence of $KHCO_3$ (C, l.c.).

Ammonium thiotungstate $(NH_4)_2WS_4$. Obtained by passing H_2S for four or five hours into a solution of 10 g. $WO_3.H_2O$ in 100 c.c. NH_4Aq S.G. .94, + 20 c.c. water, allowing to stand for some hours in a closed vessel, and washing the crystals that separate with alcohol and ether. Forms orange-yellow prisms, isomorphous with $(NH_4)_2MoS_4$; very easily decomposed "in moist air"; easily soluble in water, slightly soluble in alcohol. Heated in CO_2 gives WS_3 (B., l.c.; C, l.c.).

Ammonium dithio-oxy-tungstate $(NH_4)_2WS_5O_2$. Obtained by passing H_2S into a solution of 10 g. $WO_3.H_2O$ in 40 c.c. NH_4Aq S.G. .90, + 10 c.c. water, until the liquid becomes turbid, and washing the crystals that form with alcohol and ether. Forms yellow, prismatic crystals. When dry, the salt is unchanged in air. Decomposed by re-crystallising from water, giving paratungstate $(NH_4)_6W_{12}O_{42}.6H_2O$ (C, l.c.).

Potassium thiotungstate K_2WS_4 . Obtained by warming $(NH_4)_2WS_4$ with $KHSO_4$, adding alcohol, and crystallising from conc. $KHSO_4$. Forms yellow, prismatic needles; easily soluble in water. By continued boiling with $KHSO_4$ paratungstate is formed, $K_6W_{12}O_{42}.6H_2O$ (C, l.c.). Forms a double salt with KNO_3 , with the composition $K_2WS_4.KNO_3$ (B., l.c.).

Potassium trithio-oxy-tungstate $K_2WS_5O_2.H_2O$. Obtained in citron-yellow, quadratic tablets, by passing H_2S for three or four hours into a solution of 10 g. K_2WO_4 in 10 c.c. water, and evaporating *in vacuo*, or precipitating by alcohol (C, l.c.).

Potassium monothio-oxy-tungstate $K_2WS_3O_2.H_2O$. Obtained, in almost colourless, very hygroscopic, crystalline masses, by passing H_2S into a solution of 10 g. K_2WO_4 in 5 c.c. water until the liquid is turbid, filtering, adding 4 to 5 vols. alcohol, separating the under layer of liquid, allowing to crystallise, and washing with alcohol and ether (C, l.c.).

Sodium thiotungstate Na_2WS_4 . Obtained,

but not pure, by Corleis (l.c.), by decomposing $(NH_4)_2WS_4$ by $NaHSO_4$.

Tungsten, thiocloride of. By heating W to redness with S_2Cl_2 , Smith & Oberholzer (Zet. f. anorg. Chemie, 5, 63) obtained a red, crystalline sublimate, unstable in air, probably WS_2Cl_2 . M. M. P. M.

TUNGSTEN BRONZES v. under TUNGSTEN OXYACIDS, p. 806.

TUNGSTIC ACIDS v. TUNGSTEN OXYACIDS, p. 802; also TUNGSTEN THIO-ACIDS, *supra*.

TUNGSTOXYFLUORIDES v. under TUNGSTEN FLUORIDES, p. 799.

TUNGSTEN, ORGANIC COMPOUNDS OF. Tungsten, heated with MeI at 240° , forms WMe_4 [110°], which crystallises in tables, and is converted by Ag_2O into WMe_3O , which dissolves in acids (Litche, C. R. 42, 203; Cahours, A. 122, 70).

TUNIGIN v. ANIMAL CELLULOSE, vol. i. p. 718.

TURMERIC. The root of *Amomum Curcuma*. It contains curcumin (q. v.) and turmerol.

TURMERIC ACID $C_{11}H_8O_5$ [35°]. A product of oxidation of turmerol by cold $KMnO_4$ (Jackson & Menke, Am. 6, 77). Needles, sl. sol. water, v. sol. alcohol. — CaA' , 3aq. S. (of CaA') 1:28 at 16° . White needles. — AgA' .

TURMEROL $C_{11}H_{12}O$ (?). (193°–198° at 60 mm.). S.G. 1.1902. $[a]_D^{20} = 33.5^\circ$. An oil occurring in turmeric. Distils with decomposition at 285°–290° (Jackson & Menke, Am. 4, 368; 6, 77). Dextrorotatory. Does not combine with $NaHSO_4$. $KMnO_4$ oxidises it to acetic, terephthalic, turmeric, and apoturmeric acids. PCl_5 forms $C_{11}H_7Cl$, which is also got by heating turmerol with conc. $HClAq$ at 150° . Sodium forms $C_{11}H_7ONa$, whence isobutyl iodide forms oily $C_{11}H_{11}OC_2H_5$.

Apoturmeric acid $C_8H_6(CO_2H)_2$ (?). [221°]. Woolly mass, sol. boiling water.

TURPENTINE. Semi-fluid resins exuding from coniferous trees. They consist of resin dissolved in oil of turpentine. On distillation oil of turpentine passes over and colophony remains behind. The various oils of turpentine are described under TERPENES. The chief constituent of colophony is abietic anhydride (v. ABETIC ACID and SYLVIC ACID). On oxidation by dilute HNO_3 , colophony yields isophthalic, trimellitic, and terebic acids (Schreder, A. 172, 93). On the products of distillation of colophony v. RESINS.

TURPETHIN $C_{14}H_{18}O_4$ [c. 183°]. Occurs in the root of *Convolvulus Turpethum* (*Ipomoea Turpethum*) (Boutron-Charlard, J. Ph. 8, 131; Spirgatis, J. pr. 92, 97; A. 139, 41). Purgative yellowish-brown resin, v. sol. alcohol, insol. ether (difference from jalapin). Conc. H_2SO_4 forms a red solution. Boiling alkalis convert it into turpethic acid. Boiling dilute mineral acids yield glucose (3 mols.) and turpetholic acid (1 mol.).

Turpethic acid $C_{14}H_{18}O_6$. Amorphous yellowish mass, v. sol. water. Split up by boiling $HClAq$ into glucose and turpetholic acid. — BaA' . — $BaHA'$ (dried at 100°).

Turpetholic acid $C_{14}H_{18}O_7$ [c. 88°]. Minute needles (from dilute alcohol), sl. sol. ether. — NaA' (dried at 100°). — BaA' . Amorphous. — AgA' . Amorphous pp.

Ethyl ether EtA'. [78°]. Plates.

TYLOPHORINE. An alkaloid in *Tylophora zanthoxica* (Hooper, Ph. [3] 21, 617). Crystalline, sol. water, sol. alcohol and ether.

TYPE METAL. An alloy of 15-20 parts Sb with c. 70 parts Pb, and 10 to 15 parts Sn; v. LEAD ALLOYS, vol. iii. p. 124.

TYPES. The object of classification is to put together like things, and to put apart things that are unlike. A perfect system of chemical classification would place side by side those elements and compounds that are chemically similar, and it would also indicate the relations that exist between all the elements and all the compounds. Inasmuch as the object of chemistry is the study of the connections between composition and properties, and between changes of composition and changes of properties, a complete scheme of chemical classification must indicate the relations of the substances classified, both as regards composition and also as regards properties. To connect composition with properties necessitates a thorough knowledge of both, and this knowledge can be gained only by comparing one substance with other substances. But, because of the large amount of detailed investigation that is required before the chemical properties of an element or a compound are known, chemists have often forgotten the larger issues of their labours, and have busied themselves rather with the examination of individual bodies than with the comparative study of many bodies. And, because of the imperfection of chemical knowledge at any time, those who have attempted the classification of chemical substances have generally paid chief attention either to the composition or to the properties of the substances to be classified. Hence systems of classification have sometimes prevailed that were founded chiefly on similarities of composition, and at other times classificatory schemes have been in vogue that rested mainly on similarities of properties. But there has always been a desire, and generally an effort, to classify on the bases of composition and properties. To classify satisfactorily demands the recognition of a simple class-mark, which shall also be clear, definable, and invariably applicable. It is probably correct to say that none of the larger classes of chemical compounds has a class-mark of this description. Hence the main difficulty in chemical classification. Take, for instance, the great class of acids. What is the class-mark? What must be known about the composition of a compound before it is put into the class of acids? There is no single and sufficient class-mark to be gained by studying the compositions of acids. What, then, about the properties of acids? Here, too, no simple, definable, and applicable property has been found which serves to distinguish acids from all other compounds. Acids, it is usually said, are compounds containing *replaceable hydrogen*. But the expression replaceable hydrogen has not been, and cannot be, exactly defined. Hence, all that can be done is to set up an ideal or typical acid, and to place in the class *acids* those compounds which fairly closely approach this type as regards both properties and composition. And as with acids so with other classes of compounds. A classification by means of types becomes inevitable in such a science as chemistry,

but a typical classification cannot be final in any exact science.

Lavoisier's system of classification rested on oxygen; compounds were regarded as formed by the union of oxygen with other elements or groups of elements; the non-oxygenated part of a compound was called by Lavoisier the *rest* or *radicle*; compounds of oxygen with certain radicles were bases, compounds with other radicles were acids, and salts were formed by the union of bases with acids. Lavoisier used the term *radicle* to include elements and groups of elements.

"J'ai déjà fait observer, que dans le règne minéral presque tous les radicaux oxydables et acidifiables étoient simples; que dans le règne végétal au contraire, et surtout dans le règne animal, il n'en existoit presque pas qui ne fussent composés au moins de deux substances, d'hydrogène et de carbone; que souvent l'azote et le phosphore s'y réunissent, et qu'il en résultoit des radicaux à quatre bases."—*Traité élémentaire de Chimie*, [1793], p. 251.

About twenty-four years after Lavoisier made this statement Berzelius repeated it.

"Nachdem wir den Unterschied zwischen den Producten der organischen und der unorganischen Natur, und die verschiedene Art und Weise wie ihre entfernteren Bestandtheile untereinander verbunden sind, näher kennen gelernt, haben wir gefunden, dass dieser Unterschied eigentlich darin besteht, dass in der unorganischen Natur alle oxydierbaren Körper aus einfachen Radicalen bestehen, während hingegen alle organischen Substanzen aus Oxyden mit zusammengesetztem Radical bestehen."—*Lehrbuch der Chemie*, 2. Aufl. (Stockholm, 1817), vol. I. p. 644.

Why do acids and bases unite to form salts? What is the cause of the formation of compounds by the union of radicles, either simple or compound? These questions were answered by Berzelius by appealing to the fact that the electric current very often resolves compounds into two parts, and in many cases also effects the combination of elements or groups of elements. Radicles combine, said Berzelius, because the negative electricity on one is thereby neutralised by the positive electricity on the other. Thus arose the electro-chemical conception of dualism (v. DUALISM, vol. ii. p. 416; cf. RADICALS, vol. iv. p. 323).

In 1832 Liebig and Wöhler made an exhaustive study of compounds obtained from bitter-almond oil; they showed that the relations of composition and properties of these compounds were brought together, and expressed in a consistent conception by supposing that all the compounds contained a radicle having the composition $C_{11}H_9O$ ($C = 12, O = 16$); this group of elements, common to all the derivatives of bitter-almond oil, they called *benzoyl*. The work of Liebig and Wöhler marked a great advance in chemical classification; it was the actual working out of the connections between composition and properties of a number of compounds, and the expression of these connections in clear and definite language. The term *radicle* became henceforth the expression of a vivifying conception. The compounds derived from bitter-almond oil had certain common properties, and they had also a common composition; they belonged to the same type. The compounds of benzoyl examined by Liebig and Wöhler included such compounds as these: $C_6H_5.OH$, $C_6H_5.O.H$, $C_6H_5.O.Cl$, $C_6H_5.O.N$, $C_6H_5.O.NO$. The radicle C_6H_5O is common to all; this radicle is united with H , Cl , NO , CN , or some other radicle, in the different compounds; nevertheless

less, the properties of the compounds are so similar that all are said to belong to one type. To what extent, then, it was asked, may the properties of one radicle differ from those of another before the replacement of one of these by the other carries with it a change of type? The answer generally given to this question was: If the replacing radicle is chemically similar to the radicle replaced the type will not be destroyed. In 1834 Dumas, from the study of the action of chlorine on various organic compounds, announced the *empirical laws of substitution* as follows: (1) When a compound containing hydrogen is subjected to the dehydrogenating action of chlorine, bromine, iodine, oxygen, &c., one atom of chlorine, bromine, iodine, or oxygen, is taken up for each atom of hydrogen lost by the compound. (2) The same rule applies, without modifications, when the compound contains oxygen. (3) If a hydrogenised compound contains water the hydrogen of the water is given up without replacement, and then another quantity of hydrogen is absorbed, so that the final result is a replacement of hydrogen. A year or so later Laurent propounded a *theory of substitution*, which asserted that when equivalent substitution of hydrogen by chlorine or bromine occurs the chlorine or bromine takes the place of the hydrogen, and to a certain extent plays the same part as the hydrogen, and hence the chlorinated or brominated product must be similar to the compound from which it has been prepared. Laurent's views were much opposed, for a time by Dumas himself; but they gradually prevailed, and chemists became familiarised with the notion of the replacement of such a decidedly electro-positive element as hydrogen by an element so decidedly electro-negative as chlorine, resulting in the production of a compound of the same chemical type as the original substance.

About 1839 Dumas sought to distinguish mechanical types from chemical types. Compounds formed one from the other by the replacement of a certain number of equivalents of one radicle by the same number of equivalents of another radicle, and having their radicles similarly combined, and exhibiting similar properties, were said to belong to the same *chemical type*. Compounds were said to belong to the same *mechanical type* when they were composed of equal numbers of equivalents of radicles, but differed essentially in their properties. Dumas at this time regarded the properties of compounds as conditioned more by the arrangement than by the nature of their parts. He compared compounds to planetary systems, the planets being represented by the atoms of the compounds. One atom, he said, might be replaced by another atom, or an atom by a group of atoms, without destroying the system; if the number of replacing atoms, or radicles, were the same as the number of atoms, or radicles, replaced, and the relative arrangement of all the atoms or radicles were not altered, the compounds belonged to the same type. By some such development as this the theory of types came to include the older theory of radicles.

It is evident that the terms used by Dumas and others to express the conceptions of the theory of types are vague and incapable of

exact definition. The expression 'equivalent radicles' cannot be defined, nor can an exact and invariable connotation be given to the expressions 'radicles similarly combined' and 'compounds having similar properties.' But if it had been possible to classify chemical substances in an ideally perfect way the theory of types would not have arisen. If there is to be a typical classification the language whereby this classification is expressed must be more or less vague. Whether a compound formed from another by replacing equivalents of one kind by an equal number of equivalents of another kind does or does not belong to the same type as the parent compound can be determined only by a careful study of the properties of both compounds and by a comparison of the compounds one with another. The application of the theory of types was possible only when the properties and the compositions of compounds were exhaustively compared. The theory of types produced much fruit, because it suggested and demanded much inquiry into the fundamental problem of chemistry.

In 1849 Wurtz prepared two compounds which resembled ammonia in their prominent characters. These compounds were found to have the compositions C_2H_5N and C_4H_9N respectively ($C=6$). The similarities between the properties of these compounds and ammonia led Wurtz to regard them as *substituted ammonias*, and to express this conception by the formulæ $C_2H_5NH_2$ and $C_4H_9NH_2$. One method by which these compounds were prepared consisted in treating methyl and ethyl bromides (C_2H_5Br and C_4H_9Br ; $C=6$) with ammonia, and then decomposing the products by potash. These reactions suggested the view that the new compounds were derived from methylic and ethylic ethers (C_2H_5O and C_4H_9O , according to the notation then used) by substituting NH_2 for O . Both views agreed in representing the new compounds as $C_2H_5NH_2$ and $C_4H_9NH_2$ respectively. But the properties of the compounds resembled those of ammonia; hence the view that Wurtz's compounds were derived from ammonia prevailed. This view was expressed by saying that these compounds belonged to the ammonia type, and by comparing the formula of the typical compound with the formula of the compounds formed after that exemplar; thus:

Type:	Derivatives:
Ammonia NH_3 , H .	Methylamine NH_2 , C_2H_5 .
	Ethylamine NH_2 , C_4H_9 .

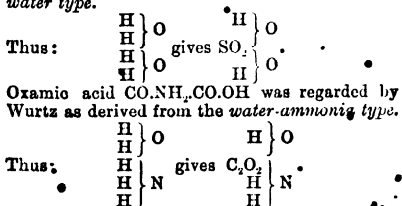
Very soon after Wurtz's preparation of methylamine and ethylamine Hofmann argued that it should be possible to substitute each of the three atoms of hydrogen in NH_3 by the radicles C_2H_5 and C_4H_9 , and so to obtain the compounds $NH(C_2H_5)_2$, $N(C_2H_5)_3$, $NH(C_4H_9)_2$, and $N(C_4H_9)_3$ ($C=6$), all which compounds ought to resemble ammonia in their properties. Hofmann fulfilled his own prophecy by preparing di- and tri-methylamine and di- and tri-ethylamine; and, basing his methods on the conception of the ammonia type, he prepared a large series of ammonia-like compounds derived from NH_3 , $2NH_3$, &c., by substituting for H various radicles composed of carbon and hydrogen. The ammonia type was thus established.

About the year 1850 Williamson studied the relations of ether to alcohol. The formula of ether was then written C_2H_5O ($C=6, O=8$), and that of alcohol $C_2H_5O_2$. Williamson heated potassium alcoholate ($C_2H_5KO_2$) with ethylic iodide (C_2H_5I), expecting to obtain ethylated alcohol ($C_4H_9(C_2H_5O)_2$); but he obtained common ether. Williamson suggested that the formula then accepted for ether should be doubled, and written $(C_2H_5)_2O_2$. He also found that by heating common alcohol with sulphuric acid, and adding methylic alcohol to the hot mixture, an ether-like compound was obtained, the simplest formula of which was C_3H_8O ($C=6, O=8$). Williamson argued that if common ether is C_2H_5O , then the ether of methylic alcohol must be C_3H_8O , and that, in the reaction of sulphuric acid with ethylic and methylic alcohols simultaneously, a mixture of these two ethers might be expected to be produced. To account for the facts he had observed Williamson proposed to double the formulae of the two ethers and to write them $(C_2H_5)_2O_2$ and $(C_3H_8)_2O_2$; and for the formula of the ether formed by the action of sulphuric acid on the two alcohols simultaneously he proposed the formula $C_5H_{12}(C_2H_5O)_2$ [$=2C_3H_8O$]. Williamson compared the relations between the alcohols and ethers with the relations between water, potash, and potassium oxide. These relations are made clearer if the formulae are expressed in terms of the atomic weights $C=12$ and $O=16$; thus:

Type:	Derivatives:
Water $H.H.O$	Alcohol $C_2H_5.H.O$
	Ether $C_2H_5.C_2H_5.O$
	Potash $K.H.O$
	Potassium oxide $K.K.O$.

Thus arose the *water type*. To this were referred such compounds as acetic acid $C_2H_3O_2.H.O$, anhydrous acetic acid $C_2H_3O_2.C_2H_3O_2$, and many others.

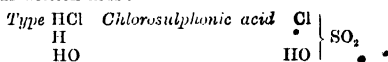
Gradually the greater number of compounds, both organic and inorganic, came to be referred to four fundamental types—the *hydrochloric acid type* HCl , the *water type* HHO , the *ammonia type* $NHHH$, and the *marsh gas type* $CHHHH$. To these were added so-called *condensed types* and *mixed types*; sulphuric acid, for instance, $SO_2.OH.OH$, was said to belong to the *double water type*.



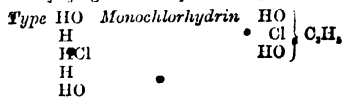
The great danger attending the development of the theory of types was, that careful investigations into the reactions of compounds might easily be abandoned in favour of a superficial examination of a compound, followed by a relegation of it to this or that type. The theory began by being very vague and elastic; the adoption of a few definite types rendered it more exact; but the temptation to manipulate for-

mulae on paper, and to invent condensed types and mixed types, gradually led chemists to see that the theory had done its work, and that it must give place to wider views, which should also be more accurate, regarding the connections between composition and properties.

The conception of types carried with it, from the first, more or less vague notions regarding the arrangements of the atoms in those collocations of atoms that form the reacting units of compounds; at any rate, this conception was bound up with the general conception of atomic arrangement. The reacting units of compounds that showed similar properties were thought of as composed of atoms similarly arranged. Moreover, the type was said to be maintained when an atom, or a group of atoms, in the parent compound was replaced by an equivalent number of atoms, or groups of atoms. These two conceptions, that of equivalency, and that of atomic arrangement, led gradually to the representation of the reacting unit, or molecule, of a compound as a definitely arranged group of atoms held together by actions and reactions between individual atoms; these conceptions led to the wider conception of valency, and to a system of classification based on the notion that each kind of atom is capable of directly combining with a limited, and determinable, number of other atoms. The formula given to chlorosulphonic acid, with the object of connecting the composition with the properties of this compound, and of suggesting relations between this and other compounds, may be taken as an example of the merging of the notion of types into that of valency. This acid was regarded as derived both from water and hydrochloric acid; it was supposed to belong to the mixed *water-hydrochloric acid type*. Hence the formula, $ClSO_2H$, was written thus:—



The radicle SO_2 was regarded as equivalent to $2H$; and it was said that the residues of the two parts of the mixed type, i.e. Cl and OH , were bound together by the radicle SO_2 . Again, monochlorhydrin, C_2H_4ClO , was regarded as a derivative of the triple type $HHO.HCl.HHO$, and was said to be formed by the binding together of the three residues OH , Cl , OH by the radicle C_2H_4 , regarded as equivalent to $3H$. Thus:—



The moment the conceptions underlying these formulae, and formulae like these, were expressed in the language of atoms and molecules, the notion of atomic valencies was gained. The group of atoms SO_2 replaces two atoms of hydrogen, one atom in the molecule HCl and one atom in the molecule HHO ; and as the atomic group SO_2 is capable of directly combining with two atoms of hydrogen, or such a number of atoms as is equivalent to two atoms of hydrogen, this group binds together the atom Cl and the atomic group OH , and so the new molecule

$\text{SO}_3\text{OH.Cl}$ is produced. This statement contains the fundamental conception of atomic valency; it also contains the conception of types, and that of radicles.

The radicles were compared as regards their equivalency, generally in terms of hydrogen; then the elementary atoms were compared, and arranged in classes, such that all in one class were exchangeable, any number of one kind for the same number of another kind.

When the atoms had been classified in accordance with the number of atoms of hydrogen, or atoms equivalent thereto, with which each was capable of combining, the foundations had been laid of a system of classification which was more accurate than that based on the notion of types, and which at the same time included the essential characters of the typical system. The article CLASSIFICATION in the first edition of this *Dictionary* represents the stage which had then (1863) been reached in the process of fusion of the theories of radicles, types, and valency. The system of classification developed in that article is based (1) on the compositions of compounds interpreted by help of the theory of valency, and (2) on the properties of the compounds interpreted by the help of the theory of types; the study of the properties of a compound is used to determine the radicles that the compound contains, and a knowledge of the valencies of these radicles determines the form of the compound, and taken along with the reactions of the compound, the type to which it is to be referred.

Although the introduction of the principle of atomic equivalency widened the conception of chemical types, it also tended towards a method of classification which was based on too slight a study of the bodies to be classified. A superficial examination of a compound generally sufficed to bring out some similarities between it and a well-known typical substance; the new compound was at once referred to its type; the form of the type determined the form of the compound under examination; it was then only necessary to manipulate the empirical formula by arranging the elements in groups, or radicles, and to assign to each radicle such a valency as satisfied the general rules that had been deduced from the study of a few typical compounds. The conception of types became very mechanical in its applications, so mechanical indeed that it was in danger of becoming metaphysical. New radicles were easily invented, and their valencies were deduced by *a priori* arguments. Kekulé recalled chemists to the study of properties by insisting that the properties of a compound are conditioned by the properties of the atoms which compose the molecule of the compound; and at a later date Mendeleëff made the same demand by asserting that the properties and the compositions of all compounds are periodic functions of the atomic weights of the elements.

The notion of types plays an important part in the classification of elements and compounds that has arisen from the practical examination of the meaning of Mendeleëff's periodic law. The periodic classification of the elements lays considerable stress on the study of the typical oxides, hydrides, hydroxides, &c., of each group of elements; for instance, the highest salt-forming oxide of Group I. belongs to the type R_2O ,

that of Group II. to the type R_2O_3 , and so on. But the word *type* is not used here with quite the same connotation as was given to it by the theory of types. All that is implied in statements such as those just made is, that the elements of Group I. combine with oxygen in the ratio of two atoms of element to a single atom of oxygen, that these oxides are salt-forming, and that they are characteristic of the elements of this group. The typical oxide-form of each group expresses the composition of that oxide which contains the greatest number of atoms of oxygen relatively to one atom of the group-element, and which oxide reacts either with acids or with alkalis to form corresponding salts. The oxides that belong to the typical oxide-form of a group may be acidic or basic, or some of them may be acidic and some basic; all that is asserted of their properties is that they are salt-forming. The properties of the typical oxide of any individual element are conditioned by the general character of the group, and the general character of the series, wherein the element is placed; by the special character of the element itself; and by the position of the element in the whole periodic system of classification. The term *type* is used in the nomenclature arising from the comparative study of the elements and compounds based on the periodic law with a wider, and at the same time a more exact, meaning than that which was given to it when the notion of types was made the basis of chemical classification. In the older classification the conception of types was the basis of the system; the conception was of necessity vague, and hence it was necessary sometimes to widen, and sometimes to narrow, the application of the conception. The modern system of classification is based on the relative weights of the atoms of the elements, and the conception of types plays a subsidiary part; the form of the typical oxide, or hydroxide, or other compound, is determined, as the compositions of all the compounds are determined, by the relative masses of the atoms of the elements; and the general character of the typical oxide, hydroxide, &c., of each group is determined, as the special character of each compound of each element is determined, also by the relative masses of the atoms of the elements.

The periodic classification of the elements and compounds makes use of the notion of types in another way, by applying the conception to certain elements. The elements placed in series 1 and 2, viz. H, Li, Be, B, C, N, O, and F, exhibit almost the whole range of properties of all the elements. The properties of the succeeding elements may almost be said to be but variations on the theme announced in the change from hydrogen to fluorine. These eight elements are types of all the others. In a somewhat narrower sense the element lithium summarises the range of properties shown in Group I.; beryllium summarises the range of properties shown in Group II.; boron, the properties of Group III.; carbon, the properties of Group IV.; nitrogen, the properties of Group V.; oxygen, the properties of Group VI.; and fluorine, the properties of Group VII. Each of the seven elements is the typical element of its group. Objections have been raised to this use of the term *typical*, on the ground that each

of the elements in question differs more from any member of its group than any other two members of the group differ from one another. But if an element is to summarise the properties of some ten or eleven other elements, it must differ considerably from each of these, while at the same time it resembles them all. The question of typical elements, and also that of typical oxide-forms, &c., are discussed in the article PERIODIC LAW (vol. iii. p. 806); that article should be consulted.

The older classification by types prepared the way for the wider conception of valency, which took up and utilised the permanent features of the typical arrangements of elements and compounds. The study of valency led chemists to see the importance of examining the properties of the atoms of the elements, and thus made them ready to accept the more elastic, and more exact, generalisation of the periodic law. The theory of types developed into the theory of valency, and the theory of valency has been included in the theory of the periodicity of the connection between the atomic weights of the elements and the compositions and properties of the compounds of the elements. The general conception of types remains; we are still obliged to picture to ourselves a typical acid, a typical base, a typical salt, a typical alcohol, a typical amide, and so on. But this conception is no longer the basis of chemical classification. We have gone deeper down, and laid the foundations of our system on the firmer basis of the atomic weights of the elements. M. M. P. M.

TYPHOTOXINE $C_8H_9NO_2$. An alkaloid obtained from pure cultures of the typhogen bacillus (Gautier, *Bl.* [2] 48, 13).

TYROSINE $C_9H_9NO_3$, i.e. $C_6H_5(OH).CH_2.CH(NH_2).CO_2H$. *p*-Oxy- α -amido-phenyl-propionic acid. Mol. w. 181. [235°]. S.G. 1.456 (Siber, B. 17, 2837). S. 0.4 at 20°; 65 at 100°. S. (90 p.c. alcohol) 0.074 in the cold. H.F. 156,400. H.C.v. 1,070,800. H.C.p. 1,071,200 (Berthelot a. André, *Bl.* [3] 4, 227). $[\alpha]_D^{20} = -8^\circ$ in HClAq at 16°; -9° in KOHAq at 20° (Mauthner, M. 3, 843).

Occurrence.—Occurs abnormally in the liver and urine (e.g. in cases of poisoning by phosphorus (Frerichs a. Städeler, J. 1855, 723; 1856, 702; Blundermann, H. 6, 242), in the cutaneous scales in pellagra (Schmetzer, *Dissert.*, Erlangen, 1862), in cochineal (De la Rue, A. 64, 35), in sprouting pumpkin seeds (Schulze a. Barbieri, J. pr. [2] 20, 401; 32, 457), in the roots of *Stachys tuberosa* (Planta, B. 23, 1699), in dahlia bulbs (Leitgeb, C. O. 1888, 1397), in alcoholic extract of woad leaves (Schunck, C. N. 37, 223), and in beetroot molasses (Lippmann, B. 17, 2835).

Formation.—1. By potash fusion from casein (Liebig, A. 57, 127; 62, 269), globulin, feathers, hairs (Leyser a. Köller, A. 83, 332), and albumen (Nencki, J. pr. [2] 17, 97).—2. By the action of boiling dilute H_2SO_4 on ox-horn (Hinterberger, A. 71, 72), on fibrin (Städeler, A. 111, 12; 116, 57), and on silk (Weyl, B. 21, 1529).—3. By putrefaction of yeast (A. Müller, J. pr. 57, 162; Bachamp, C. R. 74, 115, 184), albumen and gelatin (Jearmerek, J. pr. [2] 15, 353).—4. In small quantity by heating conglutin with HClAq (Siegfried, B. 24, 419).—5. From γ -amido-

phenyl-alanine and HNO_3 (Friedländer a. Mahly, B. 16, 854; Erlenmeyer a. Lipp, A. 219, 161).

Properties.—Stellate groups of slender silky needles (from water), insol. alcohol and ether, m. sol. NH_4Aq and KOHAq. Levorotatory. Its solution is not pptd. by lead acetate or subacetate until NH_4Aq is added. Boiling $Hg(NO_2)_2$, containing HNO_3 , turns its solution red, forming a brownish-red pp. (R. Hoffmann, A. 87, 123; L. Meyer, A. 132, 156). After warming with conc. H_2SO_4 , diluting with water, and neutralising with $BaCO_3$, the solution is turned violet by $FeCl_3$. Tyrosine gives off less N_2 when its solutions are decomposed by $NaOH$ and H_2O in presence of NH_3 than when the NH_3 is absent.

Reactions.—1. At 270° it splits up into CO_2 and $C_6H_5(OH).CH_2.CH_2.NH_2$ (Schmitt a. Nasse, A. 133, 211).—2. Potash-fusion forms *p*-oxybenzoic and acetic acids (Barth, A. 136, 110; Ost, J. pr. [2] 12, 159; Baumann, *Il.* 4, 804).—3. $KClO_4$ and $HClAq$ form tetra-chloroquinone.—4. By putrefactive fermentation it is converted into hydro-*p*-coumaric acid, and finally into *p*-cresol and phenol (Weyl, B. 12, 1450).—5. $HIAq$ and P at 150° from NH_3 and *p*-oxy-phenyl-propionic acid (Häffner, Z. [2] 4, 391; 6, 113). Conc. $HClAq$ and $HBrAq$ at 240° have no action.—6. Conc. H_2SO_4 (4 pts.) at 100° forms crystalline $C_8H_9(SO_3H)NO_3$, v. sl. sol. cold water, which also occurs in a hydrated amorphous form (containing 2aq). H_2O yields $(NH_4)HIAq$, $Ba(HIAq)$, Iaq , and $Ca(HIAq)$, 5aq (Städeler, A. 116, 57). $BaC_8H_9NO_3$ 3aq is obtained from the product of the action of H_2SO_4 (10 pts.) on tyrosine (1 pt.).—7. $MeOH$, potash, and MeI yield crystalline C_8H_9NIOK , sol. water, decomposed by warm KOHAq into NMe , and the methyl derivative of *p*-coumaric acid (Körner a. Menozzi, G. 11, 550).—8. Potassium cyanate added to boiling water containing tyrosine forms tyrosine-hydantoic acid $C_8H_9(OH).CH_2.CH(NH.CO.NH_2).CO_2H$, crystallising from water in needles, insol. ether (Jaffé, H. 7, 810). This body begins to melt at 155°, being decomposed above 170°. It gives a red colour and pp. on warming with Millon's reagent. It forms KAq , crystallising from alcohol-benzene.—9. Tyrosine administered to a dog appears in the urine as tyrosine-hydantoic acid $C_8H_9(OH).CH_2.CH(NH.CO.NH_2).CO_2H$ [275°-280°], which crystallises from water in needles, and is decomposed by heating in sealed tubes with baryta-water into CO_2 , ammonia and tyrosine. Other products found in the urine of a rabbit after a dose of tyrosine are hydro-*p*-coumaric and *p*-oxy-phenyl-acetic acids and phenols (Blundermann, H. 6, 251).

Salts.— $NaC_8H_9NO_3$.— $CaC_8H_9NO_3$.— $BaC_8H_9NO_3$ 2aq. Prisms, more sol. cold than hot water.— $Cu(C_8H_9NO_3)_2$. 8. 98 in the cold; 4 at 100°. Got by adding $Cu(OH)_2$ to a boiling solution of tyrosine (Hofmeister, A. 189, 6). Insol. alcohol. Deposits black cupric oxide on boiling with water.— $C_8H_9NO_3(HgO)$ 2aq.— $C_8H_9NO_3(HgO)$ 2aq.— $C_8H_9NO_3(HgO)$ 2aq (Vintschgau, J. 1869, 985).— $AgC_8H_9NO_3$ 2aq: amorphous pp.— $AgC_8H_9NO_3$ 2aq: crystalline powder.— $BHCl$ 2aq: needles, decomposed by water.— $BH_2P_2Cl_6$ (Gintl, Z. [2] 5, 704).— BH_2SO_4 . Slender needles, not coloured by $FeCl_3$.

Di-bromo-tyrosine $C_6H_4Br_2NO_2$, 2aq. S. 46 at 16°; 4 at 100°. Formed from dry tyrosine and Br vapour (Gorup-Besanez, A. 125, 281). Needles or tables (from water), sl. sol. alcohol. $Ag_2C_6H_4Br_2NO_2$, 2aq. — B^+HCl 1½aq. — B^+HBr . — $B^+H_2SO_4$. Prisms, sol. water and alcohol.

Nitro-tyrosine $C_6H_4N_2O_6$, i.e. $C_6H_4(NO_2)_2NO_2$. Formed from tyrosine (1 pt.), water (4 pts.), and nitric acid (4 pts. of S.G. 1.3) in the cold (Strecker, A. 73, 70; Städeler, A. 116, 77). Pale-yellow needles, sl. sol. cold water. — Salts: $Ba(C_6H_4N_2O_6)_2$ (dried at 100°). Blood-red amorphous mass. — $Ag_2C_6H_4N_2O_6$, aq.: orange pp. changing to a red powder. — B^+HCl ½aq. Tufts of lemon-yellow needles. — B^+HNO_3 . S. 20.

Lemon-yellow needles. — $B^+H_2SO_4$. Yellow needles or granules.

Di-nitro-tyrosine $C_6H_4(NO_2)_2NO_2$, [115°]. Formed by warming nitro-tyrosine with dilute HNO_3 . Golden plates (from water). — Salts: $CaC_6H_4N_2O_6$, 3aq. Golden six-sided tables. — $BaC_6H_4N_2O_6$, 2aq. Ruby-red prisms with yellow reflex, exploding when heated.

Reference. — AMIDO-TYROSINE.

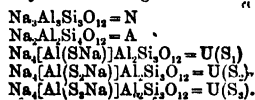
TYROTOXICON. A poisonous substance formed in milk, containing the butyric acid ferment, which has stood for some days. Occurs also sometimes in cheese (Vaughan, Ph. [3] 18, 479; H. 10, 146). When its alcoholic solution is mixed with $PtCl_4$ and evaporated violent explosion takes place.

U

ULEXINE $C_{22}H_{21}N_3O_3$. [151°]. An alkaloid in the seeds of common furze (*Ulex europaeus*) (Gerrard & Symons, Ph. [3] 17, 104, 229; 19, 1029; 20, 978, 1017). Deliquescent crystals, v. sol. chloroform, insol. ether. Poison, paralyzing respiration (Bradford, J. Physiol. 8, 79). Possibly identical with uytisine. — B^+HCl . Deliquescent. — $B^+H_2PtCl_6$. — $B^+2HAuCl_4$.

ULTRAMARINE. The blue-coloured material contained in *lapis-lazuli*. Until 1828 ultramarine was obtained by powdering and washing *lapis-lazuli*; but since that year it has been manufactured by heating to bright redness mixtures of Al silicate (*china clay*), Na_2CO_3 (carbonated soda ash), S, and charcoal, and washing, powdering, drying, and sifting the product. (For details of the manufacture v. DICTIONARY OF

APPLIED CHEMISTRY, vol. iii. p. 891.) The constituent elements of ultramarine are Al, Na, Si, S, and O. Treated with HCl aq, ultramarine gives off H_2S ; the solution contains $NaCl$, $AlCl_3$, and FeO_3 , and the residue consists of SiO_2 , S, and some Al_2O_3 ; these reactions point to ultramarine being a compound of silicates and polysulphides. Much work has been done on the constitution of ultramarine, but the results obtained have not finally settled the question. From analyses and investigations made in 1891, Brögger & Bäckström (W. J. 1891. 454) conclude that the composition of the essential colouring compound in natural ultramarine is represented by the formula $Na_4[Al(S,Na)]Al_3(SiO_3)_8$. They also conclude that artificial ultramarines may be expressed by the following formulae:—



The main constituents of the different varieties of blue ultramarine are N, A, and $U(S_1)$; of green ultramarine $U(S_2)$ and N; and $U(S_1)$ is the main constituent of white ultramarine, according to B. & B. Formulae more or less approaching those given above have been assigned to ultramarine by other observers; thus Silber in 1880 represented blue ultramarine as $Si_4Al_3Na_4S_8O_{32}$ (B. 13, 1854). On the other hand,

some chemists have regarded the essential constituent of ultramarine as a sodium thiosilicate; for instance, Rickmann (B. 11, 2013 [1878]) gives $S.Si(ONa)_2$ as the composition of 'ideal ultramarine blue'; and he regards artificial ultramarine as a mixture, the only essential part of which is sodium thiosilicate. Clarke (Am. 10, 126) suggested a formula for ultramarine which should indicate the relations of this body to various natural silicates; in this respect Clarke's formula is important (v. this vol. p. 451).

White ultramarine is obtained by completely cutting off air during the roasting of the materials; it is changed to blue by heating in O , SO_2 , or Cl (v. Ritter, W. J. 1160. 226; cf. Philipp, B. 9, 1109; 10, 1227; Böttlinger, A. 182, 311; R. Hoffmann, A. 194, 1).

Red ultramarine was observed by Scheffer, in 1873, to be formed in preparing the ordinary substance in a muffle furnace very strongly heated and freely exposed to the air; it contains less Na and more Al than the blue variety (B. 6, 1450; v. also Büchner, D. P. J. 231, 446; Zettner, B. 8, 259, 353).

Yellow ultramarine is formed by heating the red variety in the air a little above 360°, for a short time (R. Hoffmann, A. 194, 1). According to Büchner (B. 7, 990), both the yellow and red forms are produced by heating blue ultramarine to 300°–400° in O or SO_2 ; the colour changes to red and then to yellow. If Cl is passed over ultramarine before the formation of the blue variety is completed, at 410°, the colour goes green, and then reddish-yellow (Zettner, B. 8, 259, 353); by heating the product with alkali, all Cl is removed and a violet ultramarine is produced. This variety goes to the red form when heated in vapour of HNO_3 or HCl at 130°–150° (Zettner, l.c.).

Green ultramarine is formed when a little S is used in the roasting process; it is converted into the blue substance by roasting with S . This form seems to be intermediate between white and blue ultramarine. According to Philipp (B. 9, 1109), S is not taken up in the change from green to blue; by heating the green form in sealed tubes with water, at 100°, he obtained the blue, the water removing a very small quantity of sodium compounds.

Substituted ultramarines. Blue to green, and reddish-grey, substances have been formed by heating ultramarine with AgNO_3 aq. and by treating the product of this reaction with KI , LiI , BaI_2 , ZnI_2 , &c. These substances, known as *silver ultramarine*, *potassium ultramarine*, &c., probably contain Ag, K, Li, Ba, &c., in place of Na (v. Unger, *D. F.* 212, 224, 301; Philipp, *B.* 10, 1227; Heumann, *A.* 199, 253; 201, 262; Forcrand a. Ballin, *Bl.* [2] 30, 112). By heating silver ultramarine with various alcoholic iodides, Forcrand (*C. R.* 88, 30) obtained ultramarines containing alcoholic radicles, such as *ethyl ultramarine*, *amyl ultramarine*, &c. *Selenion* and *tellurium ultramarines* have also been produced, wherein S is substituted by Se or Te (v. Leykauf, *W. J.* 1876, 555; Guinet, *A. Ch.* [5] 13, 102; Plieque, *Bl.* [2] 28, 518; Morel, *Bl.* [2] 28, 522). Various substituted ultramarines have been examined by Wunder (*Chem. Zeit.* 1890, 1119). M. M. P. M.

ULMIC ACID. $\text{C}_6\text{H}_4\cdot 6\text{OH}\cdot 3$; H. 4.6-4.5; O. 29.31-5. $\text{C}_6\text{H}_4\text{O}_6$ or $\text{C}_6\text{H}_4\text{O}_7$. H.C. 1983, 200. H.F. 266, 200. Formed by action of HCl on cane sugar. Is an anhydride or mixture of anhydrides $\text{C}_6\text{H}_4\text{O}_6$ (humic anhydride) (Berthelot a. André, *Bl.* [3] 7, 441, 451). Turns yellow in air and sunlight, giving off CO_2 . The same thing happens with the humic acid extracted from vegetable mould by KOH aq. and ppd. by HCl . Dilute alkalis cause it to swell up, forming insoluble salts and a small quantity of a soluble basic salt. When conc. KOH aq. is used a salt is formed, from which two-thirds of the alkali can be removed by washing, leaving $\text{KC}_6\text{H}_4\text{O}_6$ aq. and as reconverted into the acid, $\text{C}_6\text{H}_4\text{O}_6$, by HCl aq. Ammonia converts humic anhydride (ulmic acid) into an amide-acid $\text{C}_6\text{H}_4\text{NO}_2\text{NH}_2$, whence HCl sets free $\text{C}_6\text{H}_4\text{NO}_2$.

Salts.— $\text{KC}_6\text{H}_4\text{O}_6$ aq. Hard, black, insoluble mass, yielding a brown powder. The 'ulmin' of Malaguti. Formed by shaking the anhydride with KOH (1 pt.) and water (120 pts.).— $\text{NaC}_6\text{H}_4\text{O}_6$ aq.— $\text{NaC}_6\text{H}_4\text{O}_6$ aq.

References.—HUMIC, SACCHARUMIC, and SACULMIC ACIDS.

UMBELLIC ACID $\text{C}_6\text{H}_4\text{O}_6$, i.e. [4:2:1] $\text{C}_6\text{H}_4(\text{OH})_2\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$. Mol. w. 132. Di-oxy-cinnamic acid. Formed by warming its lactone, umbelliferone with KOH aq. (Tiemann a. Reimer, *B.* 12, 994; Posen, *B.* 14, 2745). Yellowish powder. Turns brown at 240° , and decomposes below 260° . Sol. alcohol and warm water, insol. ether. Resinified by boiling its aqueous solution. Reduces warm ammoniacal AgNO_3 , forming a mirror. FeCl_3 gives a brown pp.

Methyl derivative $\text{C}_6\text{H}_4\text{O}_6$. [180°-185°]. Got by heating herniarin with alcoholic potash at 160° (Barth a. Herzig, *M.* 10, 165). Needles (from water).

(β)-Di-methyl derivative $\text{C}_6\text{H}_4(\text{OMe})_2\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$. [138°]. Formed by the action of MeI and KOH in MeOH on the methyl derivative of umbelliferone in the cold (W. Will, *B.* 16, 2115; 19, 1777). Needles, v. sol. alcohol and ether. Converted into the (β)-isomeride by boiling alone or with HCl aq. Both isomerides are reduced by sodium-amalgam to the same $\text{C}_6\text{H}_4(\text{OMe})_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, and are oxidized by KMnO_4 to the same $\text{C}_6\text{H}_4(\text{OMe})_2\text{CO}_2\text{H}$.— CaA , 2aq.: crystals.— BaA , 2aq.: needles.

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(β)-Di-methyl derivative. [184°]. Formed as above, and also by saponification of its methyl ether $\text{C}_6\text{H}_4(\text{OMe})_2\text{CH}:\text{CH}\cdot\text{CO}_2\text{Me}$ [87°], which is got by evaporating methyl-umbelliferone (1 mol.) with NaOH (2 mols.) nearly to dryness, and digesting the residue with MeI and MeOH (Tiemann a. Will, *B.* 15, 2079). Needles, sol. alcohol and ether. Sl. sol. cold water.

(α)-Di-ethyl derivative [4:2:1] $\text{C}_6\text{H}_4(\text{OEt})_2\text{C}_6\text{H}_4\text{CO}_2\text{H}$. *Di-ethyl-umbelliferic acid.* [107°]. Formed by mixing ethyl-umbelliferone (5 g.) with EtI (10 g.) and a solution of KOH (4 g.) in alcohol (Will a. Beck, *B.* 19, 1780). Small plates, v. sol. alcohol, ether, and benzene.

(β)-Di-ethyl derivative. [200°]. Formed by boiling the (α)-isomeride for some time, and also by heating ethyl-umbelliferone (10 g.) with EtI (9 g.) and a solution of Na (2 g.) in alcohol for six hours at 160° . Crystals, m. sol. alcohol, sl. sol. water.

UMBELLIFERONE $\text{C}_6\text{H}_4\text{O}_5$, i.e.

$\text{C}_6\text{H}_4(\text{OH})\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$. Mol. w. 162. [224°]. S. 1 at 100° . Formed by the dry distillation of various resins, chiefly those derived from umbelliferous plants, e.g. galbanum, sagapenum, and asafetida (Sommer a. Zwenger, *A.* 115, 15; Mössmer, *A.* 119, 260; Hlasiwetz a. Grabowski, *A.* 139, 100; Hirschsohn, *C. C.* 1877, 182). Formed by heating malic acid (1 mol.) with resorcin (1 mol.) and H_2SO_4 (Pechmann, *B.* 17, 932). Prepared by distilling the alcoholic extract of gum galbanum (Tiemann a. Reimer, *B.* 12, 993). Needles, sl. sol. cold water and ether, v. sol. alcohol. Dissolves in acids, without change. Alkalis above 50° form umbelliferic acid. Its solution in dilute alkalis shows blue fluorescence. H_2SO_4 forms a solution with green fluorescence. Reduces AgNO_3 on boiling. Yields (4,2,1)-di-oxy-benzoic acid on oxidation (Tiemann a. Parrisius, *B.* 13, 2354). Fuming HNO_3 and H_2SO_4 form $\text{C}_6\text{H}_4(\text{NO}_2)_2\text{O}_5$ [216°] (Posen, *B.* 14, 2744).

Acetyl derivative $\text{C}_{11}\text{H}_8\text{O}_6$. [140°]. Formed by acetylation, and also by boiling di-oxy-benzoic aldehyde with Ac_2O and NaOAc (Tiemann, *B.* 10, 2216; 12, 995). Needles, sl. sol. water.

Methyl derivative $\text{C}_{10}\text{H}_8\text{O}_6$, i.e. $\text{C}_6\text{H}_4(\text{OMe})\text{CH}:\text{CH}\cdot\text{CO}_2\text{H}$. [114°]. Formed by heating umbelliferone with KMe and MeI (T. a. R.). Leaflets, nearly insol. water. Appears to be identical with herniarin [118°], which is extracted by alcohol from *Herniaria hirsuta* (Barth a. Herzig, *M.* 10, 161).

Ethyl derivative $\text{C}_{11}\text{H}_{10}\text{O}_6$. [88°]. Plates, v. sol. alcohol (Will a. Beck, *B.* 19, 1779).

Oxim of the methyl derivative [4:2:1] $\text{C}_6\text{H}_4(\text{OMe})\text{CH}:\text{CH}\cdot\text{C}(\text{NOH})_2$. [138°]. Formed from the methyl derivative of thio-umbelliferone and hydroxylamine (Aldringen, *B.* 24, 8465). Needles, v. sol. hot water and alcohol. FeCl_3 colours its solution brownish-red.

Phenyl-hydrazide of the methyl derivative $\text{C}_6\text{H}_4(\text{OMe})\text{CH}:\text{CH}\cdot\text{C}(\text{NHPh})_2$. [115°]. Yellow needles, giving a blue colour with H_2SO_4 .

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Thio-umbelliferone. Methyl derivative
 $C_6H_3(OMe)<\begin{smallmatrix} CH:CH \\ O-CS \end{smallmatrix}> [114^\circ]$. Formed by heating the methyl derivative of umbelliferone with P_2S_5 (Aldringen, B. 24, 3465). Needles, sol. alcohol, v. sl. sol. water.

References.—BROMO- and METHYL-UMBELLIFERONE.

UMBELLOL $C_8H_{10}O$. (216°). V.D. 4-29. Occurs in the volatile oil of the Californian laurel (Stillmann, B. 13, 629). Oil, sol. H_2SO_4 with red colour, becoming black. Attacked by Na.

UMBELLULIC ACID v. HENDECOIC ACID.

UNDECANE v. HENDECAN.

UNDECOIC ACID v. HENDECOIC ACID.

UNDECOLIC ACID v. HENDECINOIC ACID.

UNDECYLENE v. HENDECYLENE.

UNDECYLENIC ACID v. HENDECENOIC ACID.

UNDECLIC ACID v. HENDECOIC ACID.

URACIL $CO<\begin{smallmatrix} NH.CH \\ NH.CO \end{smallmatrix}>CH$. *Di-oxy-pyrimidine*. Derivatives of this compound are formed by the action of acetone, ether on urea, thio-urea, and guanidine (Behrend, A. 229, 1; 240, 6; List, A. 236, 1; Jäger, A. 262, 365; Warrington, J. pr. [2] 47, 201).

Amido-uracil $C_4H_4N_2O_2$. Formed, together with oxuracil $C_4H_4N_2O_4$, by reducing nitro-uracil (Behrend), and by boiling di-bromo-pyruvamide with baryta-water (Fischer, A. 239, 193). Yellow needles, sol. water. Converted by cyanic acid into oxanthine $C_4H_4N_2O_4$, which crystallises in needles, sl. sol. water, sol. alkalis, gives with Cl the murexide reaction, may be oxidised to alloxantin, and gives some alloxan with bromine-water.

Acetyl derivative $C_4H_4N_2O_5$ aq. Prisms.

Nitro-uracil v. NITRO-DI-OXY-PYRIMIDINE.

Bromo-nitro-oxy-uracil. Dihydrate

$C_4H_3N_2O_3Br$ i.e. $CO<\begin{smallmatrix} NH.CH(OH) \\ NH.CO \end{smallmatrix}>CBr(NO_2)$.

Formed by adding Br to nitro-uracil suspended in water (Behrend, A. 240, 11). Crystalline mass, sl. sol. cold water and alcohol. Boiling with water produces brominated nitro-methanes and a crystalline compound $C_4H_4N_2O_4$, formed by the action of urea upon nitro-uracil. Tin and HCl reduce it to amido-uracil.

Methyl-uracil v. DI-OXY-METHYL-PYRIMIDINE.

Nitro-methyl-uracil $C_4H_4N_2O_4$. Prepared by nitrating methyl-uracil with HNO_3 (S.G. 1.5) mixed with an equal volume of H_2SO_4 (S.G. 1.84) (Behrend, A. 240, 3). Prisms or tables (from water), sl. sol. hot alcohol.

Isomeride v. NITRO-DI-OXY-METHYL-PYRIMIDINE.

Nitro-di-methyl-uracil v. NITRO-DI-OXY-METHYL-PYRIMIDINE.

Di-chloro-oxy-methyl-uracil. Dihydrate

$C_4H_3Cl_2N_2O_3$ i.e. $CO<\begin{smallmatrix} CMe(OH).NH \\ CO \end{smallmatrix}>CO$.

Formed by the action of chlorine on methyl-uracil suspended in water (Behrend, A. 236, 59). Tables (from water); slowly decomposed by boiling water. M. sol. alcohol; not decomposed by boiling alcohol. M. sol. ether. A solution of $SnCl_4$ in HCl aq. at 100° reduces it to chloro-methyl-uracil $C_4H_4ClN_2O_4$, which crystallises from water in needles. Fuming HNO_3 gives di-chloro-barbituric acid.

Di-bromo-oxy-methyl-uracil $C_4H_3N_2Br_2O_3$ i.e. $CBr_2<\begin{smallmatrix} CMe(OH).NH \\ CO \end{smallmatrix}>CO$. From methyl-uracil (or bromo-methyl-uracil), and bromine-water (Behrend, A. 229, 18; 236, 57). Cubes (from hot water). Boiling alcohol converts it into bromo-methyl-uracil $C_4H_4N_2BrO_3$. Fuming HNO_3 forms di-bromo-barbituric acid.

Di-chloro-oxy-tri-methyl-uracil. Dihydrate
 $CO<\begin{smallmatrix} NMe.CO \\ NMe.CMe(OH) \end{smallmatrix}>CCl_2$. [144°]. Formed

by passing Cl into an aqueous solution of tri-methyl-uracil (Hagen, A. 244, 14). Crystals, sl. sol. hot water. Reduced by boiling with $SnCl_4$ to chloro-tri-methyl-uracil, which crystallises in prisms, m. sol. hot water.

Nitro-ethyl-uracil v. NITRO-DI-OXY-ETHYL-PYRIMIDINE.

Methyl-ethyl-uracil v. DI-OXY-METHYL-ETHYL-PYRIMIDINE.

Nitro-methyl-ethyl-uracil v. NITRO-DI-OXY-METHYL-ETHYL-PYRIMIDINE.

Amido-uracil carboxylic acid v. DI-OXY-AMIDO-PYRIMIDINE CARBOXYLIC ACID.

References.—THIO-METHYL-URACIL and URAMIDO-CROTONIC ACID.

URAMIDO-ACETIC ACID v. HYDANTOIC ACID.

p-URAMIDO-BENZENE SULPHONIC ACID $NH_2.CO.NH.C_6H_4.SO_3H$. Formed by evaporating a solution of p-amido-benzene sulphonic acid and potassium cyanate (Pellizzari, A. 248, 156), and also by heating dry p-amido-benzene sulphonic acid (1 mol.) with urea (1½ mols.) (Friedel, C. R. 112, 868). Pearly plates (from dilute alcohol), v. sol. water. — BaA' , 3aq; monoclinic prisms, sol. aq.

o-URAMIDO-BENZOIC ACID $C_6H_4N_2O_4$ i.e. $NH_2.CO.NH.C_6H_3(CO_2H)$. Formed from potassium cyanate and the hydrochloride of o-amido-benzoic acid (Griess, J. pr. [2] 5, 371; B. 11, 1730). HNO_3 yields only one di-nitro-derivative. m-Uramido-benzoic acid $C_6H_4N_2O_4$. S. 1 at 100°. S. (96 p.c. alcohol) 72 at 16°. S. (ether) 127 at 16°. Occurs in urine after a dose of m-amido-benzoic acid (E. Salkowski, H. 7, 113).

Formation.—1. By adding potassium cyanate to a boiling saturated solution of the sulphate of m-amido-benzoic acid (Menschutkin, A. 153, 84; Z. [2] 4, 275).—2. By fusing m-amido-benzoic acid with urea (Griess, Z. [2] 5, 312; B. 2, 47). 3. By boiling m-cyanamido-benzoic acid with HCl aq (Traube, B. 15, 2122).

Properties.—Small prisms (containing aq), v. sl. sol. hot water. At 200° it yields $CO(NH.C_6H_4.CO_2H)$. On distilling m-uramido-benzoic acid (4 pts.) with P_2O_5 (1 pt.) m-amido-benzoic nitrile [54°] is formed (Griess, B. 8, 224). Boiling KOH aq splits it up into m-amido-benzoic acid, CO_2 , and NH_3 .

Salts.— NH_4A' aq. — KA' . — CaA' , 4aq. — PbA' , 2aq. — AgA' : curdy pp., becoming crystalline.

Ethyl ether EtA' . [176°]. Formed from m-amido-benzoic ether and $KCyO$ (Griess, J. pr. [2] 4, 293). Plates, sl. sol. hot water.

Amide $C_6H_4N_2O_4$. Formed from m-amido-benzamide and $KCNO$ (Menschutkin). Scales (from water), decomposed by fusion, sl. sol. alcohol.

p-Uramido-benzoic acid $C_9H_7N_3O_4$. Formed in like manner (Griess, *J. pr.* [2] 5, 369). Plates, almost insol. cold water, v. sl. sol. hot water, m. sol. hot alcohol. Yields some *p*-amido-benzonitrile [86°] on distilling with P_2O_5 — BaA' . Plates, v. e. sol. cold water.

Di-uramido-benzoic acid $C_{10}H_{10}N_4O_4$ i.e. $(NH_2.CO.NH).C_6H_4.CO_2H$. Formed by fusing di-amido-benzoic acid with urea (Griess, *B.* 2, 47). Small granules, v. sl. sol. hot water.— BaA' , (dried at 130°). Nodules, v. sol. hot water.

References.—AMIDO-, NITRO-, and OXY-URAMIDO-BENZOIC ACIDS.

URAMIDO-BENZOYL v. OXY-QUINAZOLINE.

p-URAMIDO-BENZYL-UREA $C_{10}H_{11}N_3O_4$ i.e. $NH_2.CO.NH.C_6H_4.CH_2.NH.CO.NH_2$. [197°]. *p*-**Di-uramido-toluene**. Formed by heating together *p*-amido-benzyl-amine hydrochloride (1 mol.) and KCNO (2 mols.) in aqueous solution (Amsel & Hofmann, *B.* 19, 1289). Small needles. Sol. hot water.

URAMIDO-ISOBUTYRIC ACID v. ACETON-URAMIC ACID.

o-URAMIDO-CINNAMIC ACID $C_{11}H_{11}N_3O_4$ i.e. $NH_2.CO.NH.C_6H_4.CH=CH.CO_2H$. Formed from *o*-amido-cinnamic acid and aqueous KCNO (Rothschild, *B.* 23, 3341). Sol. NH_4Aq and hot $HClAq$.

(B)-URAMIDO-CROTONIC ACID $C_8H_7N_3O_4$ i.e. $CH_3.C(NH_2.CO.NH).CH.CO_2H$. The ether is converted by $NaOHAq$ into the salt NaA' , which crystallises in needles, v. sol. water; but on adding acids to this salt di-oxy-methyl-pyrimidine $C_4H_5N_2O_2$ is produced. Methyl-uracil is reconverted by $NaOHAq$ into sodium uramido-crotonate (Behrend, *A.* 229, 5).

Ethyl ether EtA'. [166°]. Formed from acetoacetic ether and urea. Needles, v. sol. ether, m. sol. alcohol. Decomposed by warm $HClAq$ into urea, acetone, CO_2 , and alcohol. Alcohol forms $CH_3.C(NH.CO.Et).CH.CO_2Et$ [29°] (Meister, *A.* 244, 234).

Amide $CH_3.C(NH.CO.NH_2).CH.CO.NH_2$ [131°]. Crystals (containing EtOH) (Meister).

Amido-uramido-crotonic acid. Lactam.

$C_8H_7(NH_2)_2N_2O_4$ i.e. $CO < \begin{smallmatrix} NH.CMe \\ NH.CO \end{smallmatrix} > C.NH_2$ (?).

Amido-methyl-uracil. Methyl-uracil (v. Di-oxy-methyl-pyrimidine) is converted by Br in CS_2 into crystalline bromo-methyl-uracil $C_4H_5BrN_2O_2$, whence conc. NH_4Aq at 150° forms amido-methyl-uracil (Behrend, *A.* 231, 250). Satiny plates (from water), melting near 250°. Sol. alcohol. The hydrochloride is converted by potassium cyanate into oxy-methyl-xanthine $C_4H_5N_3O_2$, 2aq, crystallising from water in prisms.— $BHClAq$. Monoclinic crystals; $a:b:c = 1.629:1.2345$; $\beta = 52^\circ 57'$.— BH_2PtCl_4 , 2aq: needles, v. sol. water.

Acetyl derivative $C_8H_7(NHAc)_2N_2O_4$ 3aq. Formed from oxy-methyl-xanthine and Ac_2O at 170°. Thick trimetric prisms (from water). Decomposes near 210° without melting. Sol. alkalis and reppd. by acids.

URAMIDO-ETHANE SULPHONIC ACID

$NH_2.CO.NH.CH_2.CH_2.SO_3H$. **Taurocarbamie acid.** Occurs in small quantity in urine after a dose of taurine (E. Salkowski, *B.* 6, 744, 1901). Formed by evaporating a solution of taurine with $KCyO$. Formed also by the action of bromine-water on ethylene- ψ -thio-urea (Gabriel,

B. 22, 1142). Dimetric plates, v. sol. water, sl. sol. alcohol, insol. ether. Decomposed by baryta-water at 140° into CO_2 , taurine, and NH_3 .— BaA' : tables (from alcohol).— AgA' . Radiating tufts of crystals.

URAMIDO-HEXOIC ACID $C_{11}H_{11}N_3O_4$ i.e. $NH_2.CO.NH.CH(C_2H_5).CO_2H$. [200°]. Formed by boiling isobutyl-hydantoin with baryta-water (Pinner & Spilker, *B.* 22, 696). Needles, v. sol. alcohol and hot water.— BaA' : nodular groups of prisms.

Ethyl ether EtA'. [135°]. Formed by heating isobutyl-hydantoin with KOH and EtBr. Needles, v. sol. alcohol and hot water.

Nitrile $NH_2.CO.NH.CH(C_2H_5).CN$.

Formed by heating the cyanhydrin of isovaleric aldehyde with urea (Pinner & Lifschütz, *B.* 20, 2351). Oil, sol. alcohol and ether. On warming with $HClAq$ it yields isobutyl-hydantoin $C_4H_9CH < \begin{smallmatrix} CO.NH \\ NH.CO \end{smallmatrix} < NH.CO$ [210°].

Amide $NH_2.CO.NH.CH(C_2H_5).CO.NH_2$ [170°]. Formed from the nitrile (1 pt.) and conc. H_2SO_4 (3 pts.) in the cold. Crystals, v. sol. water and alcohol.

URAMIDO-HIPPURIC ACID $C_{10}H_{11}N_3O_4$.

Formed by fusing *m*-amido-hippuric acid with urea (Griess, *J. pr.* [2] 1, 235). Nodules, v. e. sol. hot water. Decomposed by boiling conc. $HClAq$ into glyceoll and *m*-uramido-benzoic acid.— AgA' . Crystalline pp.

URAMIDO-NITRO-AMIDO-PHENOL

$C_8H_7N_5O_4$ i.e. $C_6H_4(NO_2)(NH_2)(NH.CO.NH_2).OH$. Formed by reducing di-nitro-oxy-phenyl-urea with ammonium sulphide (Griess, *J. pr.* [2] 5, 1). Reddish-brown needles, sl. sol. hot water and alcohol.— $BHCl$: white scales.— BaA' , 3aq: steel-blue needles, v. sol. hot water. Boiling $HClAq$ converts it into amidocarboxamidop-nitrophenol $C_6H_4N_2O_6$, which yields BaA' , 2aq and $BHClAq$, and is reduced by tin and $HClAq$ to diamidocarboxamidophenol $C_6H_4N_4O_6$, which yields $BHCl$, crystallising in plates.

URAMIDO-DI-NITRO-PHENOL v. Di-nitro-oxy-phenyl-urea.

p-URAMIDO-PHENYL-ACETIC ACID $NH_2.CO.NH.C_6H_4.CH_2.CO_2H$. [174°]. Formed by boiling *p*-cyanamido-phenyl-acetic acid with $HClAq$ (Traube, *B.* 15, 2122). Small crystals (containing 1 aq), sol. water, alcohol, and ether.

α -Uramido-phenyl-acetic acid. **Ethyl ether** $NH_2.CO.NH.CHPh.CO_2Et$. [189°]. Formed by the action of aqueous $KCyO$ on the hydrochloride of α -amido-phenyl-acetic ether (Kossel, *B.* 21, 4150). V. sol. alcohol and hot water.

Nitrile $NH_2.CO.NH.CHPh.CN$. [170°]

Formed by heating the cyanhydrin of benzoic aldehyde with urea (Pinner & Lifschütz, *B.* 20, 2351). Converted by acids into $C_8H_7N_3O_4$ [182°], crystallising in scales, v. sol. alcohol and hot water.

α -URAMIDO-PHENYL-CROTONIC ACID.

Nitrile $CHPh.CH.CH(NH.CO.NH_2).CN$.

[160°]. Formed by heating urea with the cyanhydrin of cinnamic aldehyde (Pinner & Lifschütz, *B.* 20, 2351). Needles, v. sol. hot alcohol. Boiling $HClAq$ converts it into di-oxy-styryl-pyrazole (*q. v.*).

Amide $CHPh.CH.CH(NH.CO.NH_2).CO.NH_2$. Formed from the nitrile and cold conc. H_2SO_4 (Pinner & Spilker, *B.* 22, 692). Microcrystalline

powder, decomposing at 210°-220° with evolution of NH_3 . Sol. alcohol, sl. sol. hot water.

α -URAMIDO-PROPIONIC ACID $\text{C}_6\text{H}_5\text{N}_2\text{O}_5$, i.e. $\text{CH}_3\text{CH}(\text{NH.CO.NH}_2)\text{CO}_2\text{H}$. *Lacturamic acid*. [155°]. Formed by evaporating a solution of alanine sulphate mixed with KCyO (Urech, A. 165, 99). Formed also by boiling lactyl-urea with baryta-water (Heintz, A. 169, 128). Prisms, sl. sol. cold water and alcohol, insol. ether.— BaA' , aq. (dried at 100°).— $\text{PbA}'2\text{aq}$ — AgA' : needles, m. sol. water.

Nitrile $\text{CH}_3\text{CH}(\text{NH.CO.NH}_2)\text{CO}_2\text{H}$.

[106°] (Franchimont a. Klobbie, R. T. C. 7, 16).

Amide $\text{CH}_3\text{CH}(\text{NH.CO.NH}_2)\text{CO}_2\text{H}$.

[196°]. Small needles (from alcohol), sol. water.

URAMIDO-SUCCINIC ACID. *Amic acid* $\text{NH}_2\text{CO.CH}_2\text{CH}(\text{NH.CO.NH}_2)\text{CO}_2\text{H}$. [188°]

(G.); [157°] (P.). *Succinuramide*. *Amido-succinic acid*. S. 5.4 at 23°. Formed by evaporating the mixed solutions of asparagine KCyO (Guareschi, G. 7, 404; R. 10, 1747). Dextro-asparagine gives a levo-compound, while levo-asparagine gives a dextro-compound (Piutti, B. 19, 1693). Prisms, nearly in. sol. alcohol and ether. According to Piutti, the dextro- and levo-compounds both melt at 157°.

Reactions.—1. Decomposed by fusion, with formation of malylo-ureide $\text{C}_6\text{H}_5\text{N}_2\text{O}_5$ [230°-235°], which is also formed by heating urea with asparagine at 125° (Grimaux, A. Ch. [5] 11, 400) and crystallises from water in pointed rhombohedra.—2. Boiling HClAq (S.G. 1.12) forms malylo-ureidic acid $\text{C}_6\text{H}_5\text{N}_2\text{O}_5$, which is also got by heating aspartic acid with urea at 130°. Malylo-ureidic acid crystallises in prisms [215°-220°], S. 25 at 100°, which yields BaA' , aq. and is converted by heating with bromine-water into $\text{C}_6\text{H}_5\text{Br}_2\text{N}_2\text{O}_5$, S. 3 at 100°, $\text{C}_6\text{H}_5\text{Br}_2\text{N}_2\text{O}_5$, S. 25 at 100°, $\text{C}_6\text{H}_5\text{Br}_2\text{N}_2\text{O}_5$, which is v. sol. water, $\text{C}_6\text{H}_5\text{Br}_2\text{N}_2\text{O}_5$, S. c. 6 at 100°, and $\text{C}_6\text{H}_5\text{Br}_2\text{N}_2\text{O}_5$, S. 10 in the cold and c. 22 at 100°.

URAMIDO-THIO-FORMIC ACID v. THIO-ALLOPHANIC ACID.

DI-URAMIDO-TOLUENE v. URAMIDO-BENZYL-UREA.

DI- p -URAMIDO-DI- o -TOLYL-SULPHIDE

[2:1.4] $\text{S}(\text{C}_6\text{H}_4\text{Me.NH.CO.NH}_2)_2$. *Thio- p -tolyl-di-urea*. [151°] (when containing benzene of crystallisation). Formed by heating the hydrochloride of di- p -amido-di-tolyl-sulphide with KCNO (Trehlar, B. 20, 669). Crystallises from benzene in white silky needles (containing C_6H_6).

URAMIL $\text{C}_6\text{H}_5\text{N}_2\text{O}_5$, i.e.

$\text{CO} \begin{smallmatrix} \text{NH.CO} \\ \text{NH.CO} \end{smallmatrix} \text{CH.NH}_2$. *Dialuramid*, *Amido-barbituric acid*. *Amido-malonyl-urea*. *Murexan*. Mol. w. 148. Formed by boiling alloxantin with NH_4Cl (Liebig a. Wohler, A. 26, 310; Grimaux, C. R. 87, 752) and by boiling ammonium thionurate with HClAq . Formed also by reducing nitro- or nitroso-barbituric acid with HIAq (Baeyer, A. 127, 223). It is also a product of the action of acids on murexide (Beilstein, A. 107, 188).

Properties.—Silky needles, sl. sol. hot water, insol. alcohol and ether. Sol. conc. H_2SO_4 , and re-ppd. on dilution. Its alkaline solution turns red in air, forming purpurates; thus it is converted in ammoniacal solution into murexide by boiling with air or HgO . Conc. HNO_3 forms alloxan.

Bromine at 85° forms orange $\text{C}_6\text{H}_5\text{Br}_2\text{N}_2\text{O}_5$ (Mulder, B. 14, 1060).

URAMILIC ACID $\text{C}_6\text{H}_5\text{N}_2\text{O}_5$ (?). S. 14 in the cold; 33 at 100°. Formed by heating uramil with H_2SO_4 and water, or by evaporating ammonium thionurate with some H_2SO_4 (Liebig a. Wohler, A. 26, 314; Gregory, P. M. 24, 187). Transparent, four-sided prisms, sl. sol. cold water. Converted by boiling conc. HNO_3 into nitro-barbituric acid.

URANATES v. URANIUM, OXYACIDS AND SALTS OF, p. 826.

URANIUM. U. At. w. 239 (not determined with very great accuracy). Mol. w. unknown. M.P. not determined accurately; between red heat and white heat. S.G. of fused U at 15° = 18.685 (Zimmermann, B. 15, 851). S.H. at 100° = 0.276 (Z., Lc.). S.V.S. 12.8.

Historical.—In 1789 Klaproth prepared some compounds of a new element from *pitchblende*; to the characteristic element of these compounds he gave the name uranium, from *uravós* = the heavens, in allusion to the planet *Uranus* which had been discovered a few years before (Croll's A. 1789 [2] 400). The compounds of U were examined by Richter (Gehlen's A. 4, 402), Buchholz (Gehlen's A. 4, 17, 134), Lecanu (J. Ph. 9, 141; 11, 279), Brande (S. 44, 1), Berzelius (P. 1, 359), and Arfvedson (P. 1, 245). In 1840, Péligot showed that the substance supposed till then to be U was really an oxide of U (A. Ch. [3] 5, 5); P. isolated the metal, and determined the at. w. to be 120. Mendeleeff in 1872 (A. Suppl. 8, 133; cf. C. N. 41, 39 [1889]) proposed to double the at. w. of U, making it 240; this proposal was completely justified by the determination of S.H. of pure U by Zimmermann in 1882 (B. 15, 851), and by the determination of the V.D. of UCl_4 and UBr_4 (Z., A. 216, 2 [1883]).

Occurrence.—Never uncombined. A few minerals containing compounds of U are found sparsely distributed and not in large quantities; the chief of these is *pitchblende*, which consists of U_3O_8 along with SiO_2 and oxides of Sb, As, Ca, Cu, Fe, Mg, V, &c. Carbonate, sulphate, phosphate, niobate, tantalate, and various other compounds of U are also found in varying quantities in several rare minerals (v. Zimmermann, A. 232, 300; Ridden a. MacKintosh, Am. S. [3] 38, 474; Hillebrand, Am. S. [3] 38, 329; 40, 384). Lockyer (Pr. 27, 49) stated that some of the lines in the emission-spectrum of U coincide with dark lines in the solar spectrum. Hutchins a. Holden (P. M. [5] 24, 325) think there is no trustworthy evidence in favour of the existence of U in the solar atmosphere.

Preparation.—1. A mixture of UCl_4 , NaCl , and Na is strongly heated in a closed iron cylinder. Zimmermann (A. 116, 14) used a cylinder of soft iron with walls c. 3 centim. thick, bored from a larger cylinder (similar to that employed by Nilson a. Pettersson for preparing Be; B. 11, 383) fitted with a cap which could be screwed on tightly. He placed a layer of pure fused NaCl in the cylinder, then small pieces of Na (c. 3 to 4 pts. for 10 pts. UCl_4), then UCl_4 (which must be put into the cylinder as quickly as possible, as it is hygroscopic), and covered the whole with a layer of fused NaCl . Z. raised the cylinder to a white heat, kept it at

that temperature for some time, cooled, and washed the contents with dilute alkali solution, and then with water. According to Z., the metal as thus prepared is quite pure (*v. infra*).—2. Moissan (*C.R.* 116, 847) obtained U, containing from 5 to 18.5 p.c. C, by mixing the oxide prepared by strongly heating $\text{UO}_2(\text{NO}_3)_2$ with excess of charcoal, compressing the mixture in a carbon crucible, imbedding this in MgO , and heating for 10–12 minutes in an electric furnace, using a current of 60 volts and 450 amperes.

UCl_4 is obtained by heating the nitrate $\text{UO}_2(\text{NO}_3)_2$ in air, mixing the oxide thus obtained (chiefly U_3O_8) with C, and heating in a stream of Cl (*v. URANIUM TETRACHLORIDE*, p. 823). The nitrate is obtained from *pitchblende* by powdering the mineral, washing with water, drying, and washing to remove S and As, dissolving in HNO_3Aq , evaporating to dryness, dissolving in water, filtering from Fe_2O_3 , PbSO_4 , &c., evaporating a little, and allowing to crystallise. The crystals of $\text{UO}_2(\text{NO}_3)_2$ thus obtained are purified by draining in a funnel, washing with a little cold water, drying in the air, dissolving in ether in a wide-mouthed bottle, crystallising by spontaneous evaporation, and re-crystallising from hot water; the crystals of $\text{UO}_2(\text{NO}_3)_2$ are then dissolved in water so as to form a conc. solution, UO_2CO_3 is pptd. by adding $\text{H}_2\text{C}_2\text{O}_4\text{Aq}$ to this solution, the ppt. is washed with boiling water, and then decomposed by heat, and the UO_2 thus produced is digested with conc. HClAq , washed, dissolved in HNO_3Aq , and the solution is crystallised (Péligot, *A. Ch.* [3] 5, 5; 12, 258; cf. Ebelmen, *A.* 43, 286; Wertheim, *J. pr.* 29, 209).

The oxide U_3O_8 used by Zimmermann (*v. supra*) for the preparation of UCl_4 from which pure U was obtained, was prepared by him as follows. A warm solution of commercial uranium hydroxide in HClAq was saturated with H_2S ; after standing for some time the liquid was filtered off, NH_3Aq and $(\text{NH}_4)_2\text{CO}_3\text{Aq}$ were added in excess, the liquid was warmed and $(\text{NH}_4)_2\text{SAq}$ was added; after standing the liquid was filtered, saturated with HClAq , and boiled till CO_2 was removed, then mixed with NH_3Aq and $(\text{NH}_4)_2\text{SAq}$ and heated on the water-bath till most of the $(\text{NH}_4)_2\text{S}$ was removed; the ppt. of UO_2 was collected, washed, and heated over the blowpipe; the U_3O_8 thus formed was dissolved in HNO_3Aq and the solution was crystallised; the crystals of $\text{UO}_2(\text{NO}_3)_2$ were dissolved in ether, the solution was poured off from insoluble substances, evaporated to dryness, and the residue was strongly heated; the U_3O_8 which remained was again dissolved in HNO_3Aq , and the crystals that formed on evaporation were dissolved in ether, and the ethereal solution was evaporated to dryness and the residue decomposed by heating.

Properties.—A lustrous, hard, silver-white metal; S.G. 18.685 at 15° (Zimmermann, *B.* 15, 851); if UCl_4 is reduced by Na at a red heat, U is obtained as a greyish-black powder. S.H. at $100^\circ = .0276$ (Z., &c.). U is somewhat malleable, but cannot be hammered into thin plates. The emission-spectrum, obtained by the aid of electric sparks, shows only a few lines, the most marked being one in the yellow (Thalén, *A. Ch.*

[4] 18, 289). For the fluorescence, phosphorescence, and absorption-spectra of U compounds *v. Becquerel* (*A. Ch.* [4] 27, 539), also Morton A. Bolton (*Am. Ch.* 3, 361, 401). U melts towards a white heat; according to Moissan (*C.R.* 116, 1429), the metal is volatilised by heating in an electric furnace using a current of 350 amperes and 75 volts. After long standing in the air the surface of U becomes covered with a steel-blue to black film of oxide; U that has been fused burns brilliantly when heated on Pt foil in the air; pulverulent U burns at $150^\circ\text{--}170^\circ$ in the air. U combines directly with Cl or Br, also with S; the metal dissolves in dilute $\text{H}_2\text{SO}_4\text{Aq}$ or HClAq ; it is not acted on by acetic acid, nor by KOH Aq , NaOH Aq , or NH_3Aq .

The at. w. of U has been determined (1) by determining U and Cl in UCl_4 (Péligot, *A. Ch.* [3] 5, 12 [1842]; Rammelsberg, *P.* 36, 318; 56, 125 [1842]); (2) by analyses of $\text{UO}_2\text{C}_2\text{O}_4\cdot\text{H}_2\text{O}$ (Ebelmen, *A. Ch.* [3] 5, 181 [1842]; Péligot, *A. Ch.* [3] 20, 341 [1846]); (3) by analyses of $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2\cdot 2\text{H}_2\text{O}$ (Péligot, *l.c.*; Wertheim, *J. pr.* 29, 207); (4) by analyses of the double salt $\text{UO}_2\cdot\text{Na}(\text{C}_2\text{H}_3\text{O}_2)_2$ (Wertheim, *l.c.*); (5) by transforming UO_2 into U_2O_3 and $\text{UO}_2\cdot\text{Na}(\text{C}_2\text{H}_3\text{O}_2)_2$ into Na_2UO_4 (Zimmermann, *A.* 232, 117, 273 [1886]); (6) by determining S.H. of U (Zimmermann, *B.* 15, 851 [1882]); (7) by determining V.D.s of UBr_4 and UCl_4 (Z., *A.* 216, 2 [1883]).

The at. w. of U was formerly taken as c. 120; in 1872 Mendeléeff adduced reasons for doubling this value, based on a comparative study of the properties of compounds of U to which he was led by considering the periodic arrangement of the elements (*A. Suppl.* 8, 178; *C. N.* 41, 39). When the at. w. of U was taken as 120, the formulae given to the chief oxides, chlorides, and salts of this element were UO , UCl , USO , &c.; U_2O_3 ; U_2O_4 , UOCl , $\text{UO}_2(\text{NO}_3)_2$, &c.; and U was classed with the iron metals. Mendeléeff pointed out that U was very much heavier than the iron metals, that the oxide U_2O_3 did not form salts similar to those derived from Fe_2O_3 , that the salts of UO , i.e. USO , $\text{U}(\text{NO}_3)_2$, &c., were not isomorphous with the salts of MgO , FeO , NiO , &c. Mendeléeff also drew attention to the existence of a chloride which would have to be represented as U_2Cl_4 if $\text{U} = 120$, and that this chloride was obtained by heating UCl_4 in H. Mendeléeff proposed to double the value then accepted for the at. w. of U, and, following on this, to write the formulae of the chlorides, oxides, and salts as UCl_3 , UO_2 , $\text{U}(\text{SO}_4)_2$, &c.; U_2O_5 ; UO_3 , UO_2Cl_2 , $\text{UO}_2(\text{NO}_3)_2$, &c.; and UCl_4 . It was pointed out that many of these formulae are analogous to those of the corresponding compounds of Cr, Mo, and W; and it was shown that the properties of compounds of U more nearly resemble those of compounds of Cr, Mo, and W than of any other elements. Especial stress was laid by Mendeléeff on the acidic character of the highest oxide of U. Finally, Mendeléeff showed that an element with the properties of U, and an at. w. equal to c. 240, finds its proper place in Group V., series 13, of the periodic arrangement of the elements. Mendeléeff suggested that the S.H. of pure U should be determined; that the V.D. of the volatile chloride should be found; that the action of H

on the chloride then taken to be UCl_3 should be studied; that salts of the lower oxide (UO if $U=120$, UO_2 if $U=240$) should be examined, especially as regards their isomorphism with salts of ThO_2 , SnO_2 , ZrO_2 , and TeO_2 ; that the crystalline forms of corresponding compounds of MoO_3 , WO_3 , and UO_2 ($U=240$) should be studied, and that an especially thorough crystallographic examination should be made of the compounds $\text{R}_2\text{UO}_2\text{F}_6$; and that the physical properties of compounds of Cr , Mo , W , and U should be compared. Since the publication of Mendeléeff's memoir, the S.H. of U , and the V.D.s of UBr_3 and UCl_3 have been determined, the action of H on UCl_3 has been examined, and something has been done in the study of the crystalline forms of compounds of U , including those of the form $\text{R}_2\text{UO}_2\text{F}_6$; the results of all these investigations fully confirm the justness of Mendeléeff's view that the at. w. of U is c. 240, and that this element must be classed with Cr , Mo , and W . The exact value to be given to the at. w. of U has not been yet determined; Zimmermann's measurements gave 238.75 from the ratio $\text{UO}_2:\text{U}_2\text{O}_5$, and 238.67 from the ratio $\text{UO}_2:\text{Na}(\text{C}_2\text{H}_3\text{O}_2)_2:\text{Na}_2\text{UO}_4$ ($O=15.96$). The mol. w. of U is not known.

U is the last member of the even-series family of Group VI.; this family also contains, besides the elements Cr , Mo , —, and W . The chromium elements are both metallic and non-metallic in their chemical relations; they form oxides MO_3 that are acidic, and some of the lower oxides are basic. The oxide UO_2 forms some corresponding salts; a series of salts of the form UO_2X is also known, where $\text{X}=\text{SO}_4$, &c. Several series of uranates M_2UO_6 , $\text{M}_2\text{U}_2\text{O}_8$, &c., are known. The haloid compounds are JX_3 , UX_3 , and UX_5 . (For a comparison of the metals of the Cr family v. CHROMIUM GROUP OF ELEMENTS, vol. ii. p. 168; cf. CLASSIFICATION, vol. ii. p. 207.)

The atom of U is trivalent in the gaseous molecules UBr_3 and UCl_3 .

Reactions and Combinations.—1. Heated in air U is burnt to a voluminous deposit of U_3O_8 (perhaps containing also UO_2), which stops the further oxidation of the metal. Pulverulent U burns when heated in air to $150^\circ\text{--}170^\circ$. 2. U burns brilliantly when heated in chlorine, forming UCl_3 ; heated in bromine to c. 240° part of the metal is changed to UBr_3 . 3. Heated in sulphur vapour US_2 is produced. 4. It is generally said that U does not react with water; but, according to Moissan (*C. R.* 116, 347), the metal obtained by him by reducing the oxide by charcoal in an electric furnace decomposed water at the ordinary temperature; this specimen of U contained from 5 to 13.5 p.c. C . 5. U dissolves in dilute sulphuric acid, rapidly on warming, forming USO_4 , and giving off H ; pulverulent U dissolves in hot conc. H_2SO_4 , giving off SO_2 ; the compact metal is scarcely acted on by conc. H_2SO_4 . 6. U dissolves in hydrochloric acid, dilute or conc., rapidly on warming, forming a hyacinth-red solution of UCl_3 , which goes green on shaking in air, and then contains UCl_4 . 7. Conc. nitric acid, even when hot, scarcely acts on U that has been fused; the pulverulent metal is quickly oxidised by hot conc. HNO_3 to U_3O_8 . 8. Several metallic salts in solution

are reduced by U , with ppn. of the metals, e.g. HgNO_3 , AgNO_3 , CuSO_4 , SnCl_4 , PtCl_4 , AuCl_3 .

Detection and Estimation.—Uranyl salts (UO_2SO_4 , &c.) are formed by heating uranates with acids, also by the reactions of acids with UO_2 , and also by oxidising uranous salts (salts of UO). $\text{K}_2\text{FeCy}_2\text{Aq}$ gives a brownish-red pp. with uranyl salts, soluble in HClAq or in $(\text{NH}_4)_2\text{CO}_3\text{Aq}$; this reaction is said to be extremely delicate; $\text{H}_2\text{O}_2\text{Aq}$ and alcohol give a brown pp. (Fairley, *C. N.* 62, 227); carbonates give yellow pps., soluble in excess, forming yellow liquids; NaOHAq or KOHAc forms yellow pps., NH_4ClAq does not interfere with the ppn., but in presence of sugar or tartaric acid pps. are not produced. Uranous salts are produced by reducing uranyl salts in solution by Zn and HClAq . After reduction the solutions give green pps. with KOHAc or NaOHAq , the pps. becoming brown and then yellow in the air; with $(\text{NH}_4)_2\text{SAq}$ green pps. are formed, quickly becoming dark green, and black on boiling; $\text{K}_2\text{FeCy}_2\text{Aq}$ produces yellow-green pps. becoming red in the air (v. Zimmermann, *A.* 213, 285).

U is generally estimated as UO_2 or U_3O_8 (v. Zimmermann, *A.* 232, 209). Solutions may be reduced by Zn and $\text{H}_2\text{SO}_4\text{Aq}$, and then titrated with KMnO_4Aq , the quantity of O used corresponding with the change of UO to UO_2 (*Z.*, *l.c.*; v. also Bösloubeck, *J. pr.* 99, 231).

Uranium, arsenates of. A compound, probably $\text{UO}_2\text{As}_2\text{O}_7$, 4aq, is described by Rammelsberg (*P.* 59, 26). Werther (*J. pr.* 43, 321) describes $\text{UO}_2\text{H}_2\text{AsO}_4$, 3aq, and various double salts of this compound with arsenates of Ca , Cu , and Na .

Uranium, bromides of. UBr_3 is formed by heating U_3O_8 mixed with C in Br vapour; and UBr_3 by heating UBr_3 in H . Zimmermann (*A.* 216, 5) failed to obtain a compound with more Br by heating UBr_3 with Br to 230° in a sealed tube.

URANIUM TETRABROMIDE UBr_4 . (Uranous bromide.) Mol. w. 558. Prepared by strongly heating a mixture of U_3O_8 and sugar, mixing with sugar charcoal that has been heated to redness, placing the mixture in a tube, and heating it first in a stream of thoroughly dried CO_2 , and then in Br vapour, and allowing to cool in CO_2 ; the Er used must be perfectly freed from Cl , HBr , and H_2O by distillation from KBr , MnO_2 , and P_2O_5 (Zimmermann, *A.* 216, 2; Alibegoff, *A.* 232, 132; cf. Hermann, *J.* 1861, 260). UBr_4 forms black, fusible leaflets; volatile at red heat, giving a vapour with V.D. 281 (*Z.*, *l.c.*); very hygroscopic; dissolves in water, with a hissing sound, forming a green liquid.

By evaporating a solution of $\text{UO}_2\cdot x\text{H}_2\text{O}$ in HBrAq , Rammelsberg (*P.* 59, 12) obtained green crystals of hydrated UBr_3 , probably $\text{UBr}_3\cdot 8\text{H}_2\text{O}$.

URANOXYBROMIDES. (Bromoxy-uranates.) $\text{UO}_2\text{Br}\cdot 2\text{MBr}$ or $\text{M}_2\text{UO}_2\text{Br}_2$. By the reaction of HBrAq with K_2UO_4 and $(\text{NH}_4)_2\text{UO}_4$, respectively, Sendtner (*A.* 195, 325) obtained yellowish, hygroscopic tablets of the composition $\text{M}_2\text{UO}_2\text{Br}_2\cdot 2\text{H}_2\text{O}$, where $\text{M}=\text{NH}_4$ and K .

URANIUM TRIBROMIDE UBr_3 . Mol. w. not determined. Obtained by Alibegoff (*A.* 233, 119; cf. Zimmermann, *A.* 216, 5) by passing dry H over molten UBr_3 . Dark-brown needles; easily

volatilised; not changed by continued heating in H; very hygroscopic; warmed in H₂S, in complete absence of air, forms U₂S₃.

Uranium chlorides of. By heating U in Cl both UCl₄ and UCl₃ are produced; and by heating UCl₃ in H, UCl₄ is formed.

URANIUM PENTACHLORIDE UCl₅. Mol. w. not determined; formula probably molecular, from analogy of MoCl₅ and WCl₅.

Preparation.—1. By heating U in excess of Cl. —2. A slow stream of dry Cl is passed over a mixture of charcoal and any oxide of U, or UO₂Cl₂, heated to dull redness in a glass tube; dark-green octahedral crystals of UCl₄ are formed near the heated part of the tube, and in front of these needle-shaped crystals of UCl₅ are deposited, mixed with a loose brown powder, which is also UCl₄. If the stream of Cl is rapid, most of the UCl₅ is produced as a light-brown, mobile powder (Roscoe, *C. J.* [2] 12, 933).

Properties and Reactions.—UCl₅ crystallises in long, dark, needle-shaped forms; the crystals are lustrous, and reflect greenish light, in transmitted light they are dark ruby red. Both the crystals and the brown powder are very hygroscopic. Dissolves in water, with a hissing sound, forming a yellow-green liquid and giving off HCl. Decomposed to UCl₄ and Cl when heated, either alone or in CO₂ of Cl; decomposition begins at 120° in CO₂, and is complete at 235°. Heating in NH₃ probably produces a nitride (Roscoe, *l.c.*; no analyses given).

Combination.—A compound UCl₄·PCl₅ is described by Cronander (*J.* 1873. 222) as an amorphous, yellow solid; formed by heating UO₂ with excess of PCl₅ in a sealed tube for a long time.

URANIUM TETRACHLORIDE UCl₄. (*Uranous chloride*.) Mol. w. 380.48.

Preparation.—1. U is heated in Cl. —2. A mixture of charcoal and an oxide of U, or UO₂Cl₂, is heated in a slow stream of dry Cl (Péligot, *A.* 43, 258; cf. Roscoe, *C. J.* [2] 12, 933). The crystals that form nearest to the heated part of the tube are again heated in a stream of dry CO₂, whereby traces of UCl₅ are volatilised and removed (Zimmermann, *A.* 216, 8). —3. A solution of ammonium uranate in HClAq is reduced by Zn, and the solution is evaporated and crystallised. Arendt a. Knop (*C. C.* 1857. 164) reduced, by boiling the solution for 15 min. with Cu and a little PtCl₄Aq; they then filtered, saturated with H₂S, filtered, boiled off H₂S, and crystallised.

Properties and Reactions.—Dark-green, lustrous, regular octahedral crystals; volatilises at red heat, in complete absence of moisture, giving a red vapour (Péligot, *l.c.*) with V.D. 192 (Zimmermann, *l.c.*). Very deliquescent; fumes much in air, giving off HCl; dissolves in water, with a hissing sound, forming a green solution that is unchanged in air; gives green, amorphous UCl₃ by evaporation *in vacuo*, but is decomposed by evaporation in the air. When UCl₄Aq is dropped into boiling water all the U is pptd. as UO₂·2H₂O. Solution of UCl₄ reduces salts of Au and Ag to the metals, and FeCl₃ to FeCl₂, &c. By heating in dry H one-fourth of the Cl is removed and UCl₃ remains (Péligot, *A.* 43, 266). According to Péligot (*l.c.*), UCl₄ com-

bines with several metallic chlorides to form double salts.

Uranoychlorides. (Chloroxyuranates.) UO₂Cl₂·2MCl₂·2aq, or M₂UO₂Cl₄·2aq. Salts of this composition, M = NH₄ and K, are produced by the reaction of large excess of HClAq with uranates of NH₄ and K (Péligot, *A.* 43, 279). The K compound is also formed by acting on UO₂Cl₂ with excess of KClAq, and separating the KCl that crystallises with the K₂UO₂Cl₄ mechanically (Berzelius, *P.* 1, 366). The K compound forms thick plates (for crystalline measurements *cf.* de la Provostaye, *A. Ch.* [3] 6, 165); easily loses water; gives off HCl at a little above 100°; melts at red heat, giving off Cl, and leaving UO₂ and KCl. The ammonium compound forms very deliquescent rhombohedra.

URANIUM TRICHLORIDE UCl₃. Mol. w. not determined. Obtained by Péligot (*l.c.*) by heating UCl₄ in dry H as long as HCl was given off. Also formed in solution by long-continued reduction of uranyl salts by Zn and HClAq (Zimmermann, *A.* 213, 300). A brownish-red solid; dissolves very readily in water, forming a red solution, which gives off H and becomes green (*v. P.*, *l.c.*; *Z.*, *l.c.*; also *A.* 216, 12).

Uranium ferrocyanides of. Various compounds are described by Wyrnhoff (*A. Ch.* [5] 8, 444) and Atterberg (*Bl.* [2] 24, 355) as obtained by pptg. K₂FeCy₄Aq by solutions of salts of U. The following formulae are given:

- (1) U₂FeCy₄·10aq; (2) U₂K₂FeCy₄·6aq;
- (3) (UO₂)₂K₂(FeCy₄)₂·6aq;
- (4) (UO₂)₂K₂(FeCy₄)₂·12aq.

Uranium fluorides of. Only one compound, UF₄, has been isolated with certainty.

URANIUM TETRAFLUORIDE UF₄. (*Uranous fluoride*.) Mol. w. not determined; formula probably molecular, from analogy of UBr₄ and UCl₄. Prepared by adding HFAq to U₂O₃, boiling, pouring off the yellow solution (which contains UO₂F₂), washing the green powder that remains, first on a filter and then by decantation, until free from HFAq, and drying at 100° (Smithells, *C. J.* 43, 125; cf. Bolton, *Z.* [2] 2, 353). The process of washing is very tedious, and occupies many days. UF₄ is a green powder; insol. in water and dilute acids; slowly dissolved by conc. acids; boiling NaOHaq produces UO₂. Heated in a Pt crucible with the lid on, a small quantity of a white, bulky sublimate is obtained; this sublimate is UO₂F₂ (Smithells, *l.c.*); the residue in the crucible is chiefly UO₂. Heated on Pt foil, UF₄ leaves U₂O₃ (*S.*, *l.c.*).

Double salts. Bolton (*l.c.*) obtained the compounds UF₄·KF and UF₄·NaF—as green powders, insoluble in water and dilute acids, giving UO₂, KF (or NaF), and HF when heated to redness, in closed vessels—by the action of formic or oxalic acid a. UO₂F₂·3KF or UO₂F₂·NaF (*v. infra*) in sunlight. These compounds may be called *uranofluorides*, and written KUF₄ and NaUF₄.

Uranium hexafluoride UF₆. was said by Ditte (*C. R.* 91, 116) to be formed by heating U₂O₃ with HFAq, evaporating the yellow liquid, and heating the crystals of UF₄·8HF thus obtained; but Smithells (*C. J.* 43, 125) has shown that the substance obtained by evaporating the

solution formed by heating U_3O_8 with HFAq is UO_2F_2 (v. URANIUM OXYFLUORIDE, p. 828).

Uranoxyfluorides. (*Fluoroy-uranates.*) These compounds may be regarded either as double salts of UO_2F_2 with alkali fluorides, or as salts derived from hypothetical acids $\text{H}_x\text{UO}_x\text{F}_y$. The compounds are formed by adding alkali fluorides to solutions of uranous nitrate, and crystallising under different conditions (v. Bolton, *Z.* [2] 2, 353; Baker, *C. J.* 85, 763). The compounds that have been isolated belong to several series: (1) $\text{MF.UO}_2\text{F}_2 \cdot x\text{aq} = \text{MUO}_2\text{F}_2 \cdot x\text{aq}$, where $\text{M} = \text{Na}$ and $x = 2$ and 4 (Bolton); (2) $3\text{MF.UO}_2\text{F}_2 = \text{M}_3\text{UO}_6\text{F}_6$, where $\text{M} = \text{NH}_4$ and K (Bolton; Baker); (3) $3\text{KF.2UO}_2\text{F}_2 \cdot 2\text{aq} = \text{K}_3\text{U}_2\text{O}_7\text{F}_8 \cdot 2\text{aq}$ (Baker); (4) $5\text{KF.2UO}_2\text{F}_2 = \text{K}_5\text{U}_2\text{O}_7\text{F}_8$ (Baker); (5) $82\text{BaF}_2 \cdot 5\text{UO}_2\text{F}_2 \cdot 2\text{aq}$ (Bolton). Two other series were described by Ditte (*C. R.* 91, 166), $4\text{MF.UO}_2\text{F}_2$ and $4\text{MF.UOF}_3 \cdot x\text{aq}$; but the experiments of Smithells (*C. J.* 48, 131) have shown that these compounds do not exist.

Uranium, haloid compounds of. U combines directly with Br and Cl, but not with I; no iodide, indeed, has been isolated. The haloid compounds of U belong to the form UX_n , where $\text{X} = \text{Br}$ or Cl ; UX_n , where $\text{X} = \text{Br}$, Cl or F ; and UX_3 , where $\text{X} = \text{Cl}$. The compounds UBr_3 and UCl_3 have been gasified, and the formulae are molecular. From the analogy of WCl_3 and MoCl_3 , the formula UCl_3 is probably molecular; this compound decomposes to UCl_4 and Cl when heated, either alone or in CO_2 or Cl . From the analogy of CrCl_3 , it may be supposed that UCl_3 and UBr_3 are molecular formulae. No haloid compounds of U have been isolated corresponding with the chlorides of Cr, Mo, and W, M_2Cl_6 . No haloid compounds of U are known containing each more than one halogen. Various oxyhaloid compounds, chiefly UO_2X_2 , and compounds of these with alkali haloids, are known.

Uranium, hydroxides of, v. URANIUM, OXIDES AND HYDRATED OXIDES OF (infra); also URANIUM OXYACIDS, AND SALTS OF (p. 826).

Uranium, iodides of. No compound of U and I has been isolated. Hermann (*J.* 1861, 286) and Sendter (*Verbind. des Uraniums*, Erlangen, 1877) failed to obtain an iodide by heating a mixture of UO_2 and C in I vapour or in HI.

Uranium, nitride of, U_3N_4 . A greyish-black powder; obtained by heating UCl_3 in NH_3 , then mixing with NH_4Cl and heating for a long time in a stream of NH_3 (Uhrlaub, *Verbind. einiger Metalle mit Stickstoff*, Göttingen, 1855). Roscoe (*C. J.* [2] 12, 933) states that a nitride is formed by heating UCl_3 in NH_3 , but no analyses are given.

Uranium, oxides and hydrated oxides of. When U is burnt in air the product is U_3O_8 ; by heating this oxide with reducers, or for a long time in a stream of N or CO_2 , UO_2 is formed; UO_2 is produced by fusing U_3O_8 with KClO_4 , also by heating $\text{UCl}_3(\text{NO}_3)_2$; by adding $\text{H}_2\text{O}_2\text{Aq}$ to $\text{UO}_2(\text{Q.E.O.})_2\text{Aq}$ or $\text{UO}_2(\text{NO}_3)_2\text{Aq}$ a hydrate of UO_2 is obtained. Besides these four oxides, others, intermediate between UO_2 and U_3O_8 , perhaps exist. No definite hydrate of UO_2 has been isolated; the pp. formed by adding NH_4Aq to UCl_3Aq , or to solution of a uranous salt ($\text{U}(\text{SO}_4)_2$, &c.), is either a hydrate, or a

mixture of hydrates, of UO_2 . A hexahydrate of U_3O_8 probably exists. Uranic acid is the monohydrate of UO_2 . UO_2 dissolves in some acids to form corresponding salts; U_3O_8 is said to react with conc. H_2SO_4 or HClAq to form both uranous salts UX_n , and uranyl salts UO_2X , where X = a divalent acidic radicle. UO_2 interacts with several acids to form uranyl salts UO_2X^{11} ; UO_2 also reacts as an acidic oxide with strong bases, forming uranates, di-uranates, &c., M_2UO_4 , $\text{M}_2\text{U}_2\text{O}_7$, &c.

According to Guyard (*B.* [2] 1, 89), two oxides having the compositions UO and U_2O_3 exist; but the more accurate investigations of Zimmermann (*A.* 213, 301) showed that the substances examined by Guyard were not definite compounds. Pélégot described a "black oxide U_2O_3 "; Zimmermann (*A.* 232, 273) has shown that the substance is a mixture, in variable proportions, of UO and U_2O_3 .

URANIUM DIOXIDE UO_2 . (*Uranous oxide.*) Mol. w. not known. This oxide was supposed to be the element U until 1840, when Pélégot proved the presence of O in the substance (*A. Ch.* [3] 5, 5).

Formation.—1. By heating U_3O_8 with such reducing agents as H (Arfvedson, *P.* 1, 245), NH_4Cl and S (Hermann, *J.* 1861, 258), a little C (Buchholz, *Gehülfs Ann.* 4, 17, 134), oxalic acid (Wertheim, *J. pr.* 20, 211), &c.—2. By heating U_3O_8 for a long time in a stream of N or CO_2 (Zimmermann, *A.* 232, 293).—3. By strongly heating $\text{UO}_2\text{C}_2\text{O}_4$ in absence of air (Berzelius, *P.* 1, 359), or in a stream of H (Pélégot, *A. Ch.* [3] 5, 5; Ebelmed, *A. Ch.* [3] 5, 189).

Preparation.—A mixture of UO_2Cl_2 and excess of NaCl and NH_4Cl is strongly heated in absence of air; and the product is washed thoroughly with water, and dried (Wöhler, *Z.* 41, 345; cf. Hillebrand, *Zeit. f. anorg. Chemie*, 3, 243). If air is not excluded during heating, some UO_3 is obtained (H., *l.c.*). This process gives UO_2 as a black crystalline powder. In place of using UO_2Cl_2 , a solution of ammonium uranate in HClAq may be mixed with excess of NaCl and NH_4Cl , and evaporated to dryness, and the residue heated. By fusing any oxide of U with borax for 24 hours, and washing with water and then with dilute acetic acid, or dilute HClAq , Hillebrand (*l.c.* p. 249) obtained jet-black octahedra of UO_2 isomorphous with ThO_2 .

Properties.—Prepared by heating $\text{UO}_2\text{C}_2\text{O}_4$, UO_2 is a dark-brown, pyrophoric powder; if the temperature has been kept high the oxide is lustrous, reddish-black, and not pyrophoric; prepared by heating UO_2Cl_2 with NaCl and NH_4Cl , UO_2 forms black, non-pyrophoric, octahedral crystals. Pélégot gave S.G. 10.15; according to Hillebrand (*l.c.*), the S.G. is nearly 11. UO_2 is insoluble in water, HClAq , and dilute $\text{H}_2\text{SO}_4\text{Aq}$; it dissolves in HNO_3Aq , and in conc. H_2SO_4 in presence of a little water. UO_2 is oxidised to U_3O_8 by heating in air.

Reactions.—1. Heated in air or oxygen U_3O_8 is produced; UO_2 burns brilliantly in the $\text{O}_2\text{-H}$ flame (Clarke, *G.* 4, 62, 553).—2. Heating in chlorine produces UO_2Cl_2 ; when mixed with carbon and heated in chlorine, UCl_4 and UCl_3 are formed. UBr_3 is produced by heating UO_2 mixed with carbon in bromine vapour.—3. U_2O_3 is formed by heating UO_2 in water vapour

(Regnault, *A. Ch.* [2] 62, 358).—4. Heating in vapour of carbon disulphide produces $U_2O_3S_2$ (Hermann, *J.* 1861. 258; H. Rose, *G. A.* 73, 139). UO_2 is said to be unchanged by heating in *hydrosulphide* (Arfvedson, *P.* 1, 245).—5. A solution of UO_2 in conc. sulphuric acid gives green crystals of $U(SO_4)_2$ on evaporation.

HYDRATES OF URANIUM DIOXIDE. No definite hydrate of UO_2 has been isolated; NH_4Aq produces a reddish-brown pp. when added to UCl_4Aq or solution of a uranous salt, this pp. becomes black on boiling; when washed with air-free water and dried *in vacuo* it forms black, coherent lumps. A black pp. is also produced by dropping UCl_4Aq into boiling water. These black pps. contain UO_2 ; they are probably hydrates of this oxide. The name *uranous hydroxide* is often given to the pp. obtained by either of the processes described; the pp. dissolves in dilute H_2SO_4Aq , HNO_3Aq , and $HClAq$.

URANOSO-URANIC OXIDE U_2O_5 . (*Olive-green oxide of uranium.* *Uranyl uranate* $UO_2 \cdot 2UO_3$.) Mol. w. not known.

Occurrence.—In combination with SiO_2 , and oxides of Sb, As, Ca, Cu, Fe, Mg, &c., in *pitchblende*.

Preparation.—U, or a decomposable U compound, e.g. $UO_2(NO_3)_2$, is heated in the air and then in a stream of O_2 , and is allowed to cool in O_2 (v. Zimmernmann, *A.* 232, 283). For a method of preparing U_2O_5 from *pitchblende* v. URANIUM, *Preparation* of (p. 831).

Properties.—A dark olive-green powder, sometimes almost black, but always showing a green streak when rubbed on unglazed porcelain (Z., *l.c.*). S.G. 7.2 (Karsten, *S.* 65, 394); 7.31 (Ebelmen, *J.* pr. 27, 385). S.H. -0.7979 (Donath, *B.* 12, 742). Insoluble in water; slightly soluble in dilute $HClAq$ or H_2SO_4Aq ; soluble in HNO_3Aq , also in H_2SO_4 with a little water.

Reactions.—1. Gives off O when heated in air or in an indifferent gas; the final product of heating in N or CO_2 is UO_2 (Zimmernmann, *A.* 232, 283).—2. Reduced to UO_2 by heating with hydrogen, carbon, sulphur, potassium, or sodium. 3. Heated in vapour of carbon disulphide $U_2O_3S_2$ is formed.—4. Heated with conc. sulphuric acid, or with hydrochloric acid to 180° – 200° , gives both uranous and uranyl sulphates, or chlorides; reacting as $UO_2 \cdot 2UO_3$ (Z., *A.* 232, 287).—5. Silver nitrate solution is slowly reduced to Ag (Isambert, *C. R.* 80, 1089).

HYDRATE OF URANOSO-URANIC OXIDE. By adding NH_4Aq to UCl_4Aq and allowing the pp. to oxidise in the air, and drying *in vacuo* over H_2SO_4 , Rammelsberg (*P.* 55, 319) obtained a greenish-black solid which may have been a hydrate of U_2O_5 ; one determination of water only is given which agrees fairly with $U_2O_5 \cdot 6aq$.

URANIUM TRIOXIDE UO_3 . (*Uranic anhydride.* *Uranyl oxide* $(UO_3)_2$.) Mol. w. not known. This oxide is obtained by carefully heating the hydrate $UO_3 \cdot H_2O$ (v. *infra*) to 800° (Ebelmen, *A. Ch.* [2] 5, 199); to 250° , temperature being gradually raised (Jacquelin, *Ph. C.* 1845, 183). The oxide is also formed by heating $UO_2 \cdot CO_2 \cdot 2(NH_4)_2CO_3$ to 800° (E., *l.c.*). The preparation of UO_3 may be conducted by heating $UO_2(NO_3)_2$ in a Pt basin until decomposition begins, then transferring to glass tubes

and heating these in an oil-bath to 250° so long as acid fumes are given off.

UO_3 is a chamois-yellow powder. S.G. 5.02 to 5.26 (Brauner & Watts, *P. M.* [5] 11, 60). Ebelmen (*l.c.*) described UO_3 obtained by heating $UO_2 \cdot CO_2 \cdot 2(NH_4)_2CO_3$ as a sealing-wax-red powder. When UO_3 is heated to redness it gives off O and U_2O_5 remains (E., *l.c.*; cf. Read, *C. J.* 65, 313 [1894]); the oxide seems to be somewhat volatile at the temperature of a porcelain oven (Elsner, *J.* 1866, 35).

UO_3 reacts with many acids as a basic oxide, but the salts formed are always basic salts of the forms $UX_{n-2}UO_3$, where X = the radicle of a monobasic acid, and $UX_{n-2}2UO_3$, where X = the radicle of a dibasic acid. It is customary to write the formulae of these basic salts as $UO_3 \cdot X_2$ and $UO_3 \cdot X_2$, and to call them *uranyl salts*

(UO_3 = uranyl); thus $U(NO_3)_2 \cdot 2UO_3 = UO_3(NO_3)_2$, and $U(SO_4)_2 \cdot 2UO_3 = UO_3(SO_4)_2$.

UO_3 behaves towards strong bases as an acidic oxide, forming uranates M_2UO_6 , and diuranates $M_2U_2O_7$, &c.; these salts are generally formed by fusing U compounds with bases and O , and by ppg. uranyl salt solutions by strong bases. When $KOHAq$, $NaOHAq$, NH_4Aq , $BaOHAq$, or $CaOHAq$ is added to a solution of uranyl salt, e.g. to $UO_3(NO_3)_2Aq$, the pp. consists of a uranate of the metal of the base. Alkali carbonates ppt. alkali uranates, but the pps. contain also CO_2 ; the pps. dissolve in excess of the alkali carbonates forming double carbonates of uranyl and the alkali metal, e.g. $UO_3 \cdot CO_3 \cdot 2(NH_4)_2CO_3$. Addition of alkali or alkali carbonate to solutions of uranyl salts containing other metallic salts causes pptn. of a uranate of the metal of the salt present, generally mixed with alkali uranate (cf. URANIUM, OXYACIDS, AND SALTS THEREOF, p. 826).

By adding KOH to a cold solution of UCl_4 or $UO_3(NO_3)_2$, and dialysing, Graham (*T.* 1861, 213) obtained a solution, free from acid and alkali, which he regarded as a loose compound of sugar and UO_3 , and which he called *sucrate of peroxide of uranium*.

HYDRATES OF URANIUM TRIOXIDE. Pure hydrates of UO_3 are not obtained by ppg. uranyl salt solutions by alkalis (v. *supra*); but according to Ebelmen (*A. Ch.* [3] 5, 199) $UO_3 \cdot xH_2O$ is produced by boiling an aqueous solution of $UO_2 \cdot CO_3 \cdot 2(NH_4)_2CO_3$ until a yellow pp. is formed, and allowing this pp. to stand for a long time. By the continued action of sunlight on $UO_3(C_2O_4)_2$ in presence of water, $UO_3 \cdot xH_2O$ is said to be formed; after washing and drying in the air, the solid has the composition $UO_3 \cdot 2H_2O$; and after drying *in vacuo* the composition is $UO_3 \cdot H_2O$ (E., *l.c.*). Berzelius (*B. J.* 24, 118) obtained $UO_3 \cdot H_2O$ by heating $UO_3(NO_3)_2$ on a sand-bath until acid fumes ceased to be given off, washing the residue with boiling water, and drying in air. The same hydrate is said to be formed by heating UO_3 with $KClO_4$ until fusion begins, boiling out with water, and drying in air (Druckmann, *J.* 1861, 250). The best method of preparing $UO_3 \cdot H_2O$ seems to be that given by Malaguti (*A. Ch.* [8] 9, 463), viz. boiling a solution of $UO_3(NO_3)_2$ in absolute alcohol as long as a

reaction proceeds, washing the yellow solid that separates with water, and drying in air or *in vacuo*; EtNO_3 , N_2O_5 , $\text{C}_2\text{H}_5\text{O}$, and H_2CO_3 are formed in the reaction.

$\text{UO}_2\cdot\text{H}_2\text{O}$ is described as a yellow powder; S.G. 5.98 at 15° (Malaguti, *l.c.*); reddens litmus paper; when hot it absorbs CO_2 from the air; heated to 250° – 300° water is given off and UO_2 remains (Ebelmen, *l.c.*; Jacquelin, *A. Ch.* [3] 5, 199); heated to redness gives off O and leaves U_3O_8 . $\text{UO}_2\cdot\text{H}_2\text{O}$ is generally called *uranic acid*; v. URANIUM OXYACIDS, AND SALTS THEREOF (*infra*).

URANIUM PEROXIDE. By adding $\text{UO}_2(\text{NO}_3)_2\cdot\text{Aq}$ to a mixture of $\text{H}_2\text{O}_2\cdot\text{Aq}$ and a large excess of $\text{H}_2\text{SO}_4\cdot\text{Aq}$, and allowing to stand for a considerable time, Fairley (*C. J.* 31, 13 (1877)) obtained a small quantity of a heavy, crystalline, almost white ppt., which when dried (? in air, or at 100°) had the composition UO_4 . By adding dilute $\text{H}_2\text{O}_2\cdot\text{Aq}$ to solution of $\text{UO}_2(\text{NO}_3)_2$ or $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2$, free from acids, Fairley (*l.c.* p. 127) obtained a yellowish-white ppt., which when dried by pressure between filter paper had the composition $\text{UO}_4\cdot\text{H}_2\text{O}$, and when dried at 500° the composition $\text{UO}_4\cdot 2\text{H}_2\text{O}$.

Zimmermann (*A.* 232, 273 [1886]) failed to obtain the tetrahydrate $\text{UO}_4\cdot 4\text{H}_2\text{O}$; according to him the dihydrate $\text{UO}_4\cdot 2\text{H}_2\text{O}$ is very hygroscopic, and begins to decompose at 115° . Alibegoff also obtained only $\text{UO}_4\cdot 2\text{H}_2\text{O}$; he failed to prepare the anhydrous oxide UO_4 (*A.* 233, 123 [1886]).

Hydrated uranium peroxide, dried at 100° , is a yellowish-white powder; decomposed by heat, giving off O and leaving much U_3O_8 ; reacts with alkali solutions to give $\text{UO}_2\cdot x\text{H}_2\text{O}$, and a solution from which alkali *peruranate* $2\text{M}_2\text{O}\cdot\text{UO}_4\cdot 8\text{aq}$ crystallises (Fairley, *l.c.*; v. *Peruranates* under URANIUM OXYACIDS, AND SALTS THEREOF, p. 827).

URANIUM OXYACIDS, AND SALTS THEREOF. $\text{UO}_2\cdot\text{H}_2\text{O} = \text{H}_2\text{UO}_4$ reacts with strong bases as an acid, forming uranates M_2UO_4 ; di-uranates $\text{M}'_2\text{U}_2\text{O}_7$ are also known, and a few tri- and hexa-uranates. A few peruranates are derived from hydrated uranium peroxide $\text{UO}_4\cdot x\text{H}_2\text{O}$. The compounds of $\text{UO}_2\cdot\text{X}_2$ with MX (X = Br, Cl, or F) may be regarded as bromoxy-, chloroxy-, and fluoxy-uranates. The substance known as *uranium red* is perhaps $\text{UO}_2\cdot\text{ONH}_4\cdot\text{SNH}_4$, i.e. the ammonium salt of an oxythio-uronic acid (v. URANIUM OXSULPHIDES, p. 828).

URANIC ACID H_2UO_4 . This compound is obtained as a yellow powder, which reddens litmus paper, and is decomposed to UO_2 and H_2O at 250° – 300° , and to U_3O_8 and O at a higher temperature, by boiling a solution of $\text{UO}_2(\text{NO}_3)_2$ in absolute alcohol, washing the solid that separates with water, and drying in air or *in vacuo*. (For other methods of preparation, and more details v. HYDRATES OF URANIUM TRIOXIDE, p. 825.) The salts of H_2UO_4 are prepared indirectly.

URANATES, DI-URANATES, &c. Salts derived from H_2UO_4 , salts derived from the hypothetical acids $\text{H}_2\text{U}_2\text{O}_7$, $\text{H}_2\text{U}_3\text{O}_{10}$, $\text{H}_2\text{U}_4\text{O}_{13}$, are also known.

URANATES. Salts of the composition $\text{M}'_2\text{UO}_4$ and $\text{M}''\text{UO}_4$. These salts are prepared by ppg. solutions of uranyl salts by bases in solution, or by adding alkali solution to a mix-

ture of a uranyl salt and a metallic oxide in solution; also, in many cases, by oxidising U_3O_8 or UO_2 in presence of a base or a salt of a base. The uranates are insoluble in water, and are not readily decomposed by heat except the ammonium salt. Carson and Norton (*Am.* 10, 219) have pointed out that analyses of uranates always show considerable differences between the percentages of U found and calculated; they have found the same anomaly in analyses of uranates of ammonium and several ammonium derivatives, such as NEtH_4 , NEt_2H_3 , &c.

Ammonium uranates. The pure salt does not seem to have been isolated. An impure uranate containing c. 90 p.c. UO_2 ($(\text{NH}_4)_2\text{UO}_4$ requires 84.66 p.c. UO_2) is obtained by adding NH_4Aq to a solution of a uranyl salt (Féligot); it is a yellow powder, which loses H_2O and NH_3 above 100° , very slightly soluble in water, and insol. NH_4Aq (Arfvedson, P. 1, 245). An impure salt is also obtained by adding NH_4ClAq or $(\text{NH}_4)_2\text{SO}_4\text{Aq}$ to boiling $\text{Na}_2\text{UO}_4\text{Aq}$, as long as NH_3 and CO_2 are given off, washing the ppt., and drying at a low temperature (Anthon, D. P. J. 156, 211). Heated to redness gives U_3O_8 ; many of the compounds of U are prepared from ammonium uranate.

Potassium uranate K_2UO_4 . Prepared by heating 6 g. U_3O_8 with HClAq and HNO_3Aq , adding 4 g. KCl and 16 g. NH_4Cl , evaporating to dryness, heating very strongly until the fused mass is orange-yellow, and washing with water (Zimmermann, A. 213, 290). The salt is said to be formed also by strongly heating UO_2HPO_4 (obtained by ppg. a uranyl salt by a phosphate) with K_2SO_4 (Grandeau, A. Ch. [6] 8, 223). Orange-yellow, rhombic tablets; insol. water, cold or hot; easily sol. acids (Zimmermann, *l.c.*).

Sodium uranate Na_2UO_4 . Prepared by fusing U_3O_8 with NaCl and Na_2CO_3 , or with NaCl with gradual addition of NaClO_4 , and washing with water; resembles K_2UO_4 (Zimmermann, *l.c.*).

Lithium uranate Li_2UO_4 has been prepared similarly to K_2UO_4 ; it is said to be decomposed by hot water (*Z.*, *l.c.*). Uranates of Ba, Ca, and Sr— MUO_4 —are said by Ditte (*C. R.* 95, 988) to be formed by heating the chlorides of these metals with U_3O_8 .

DI-URANATES. Salts of the composition $\text{M}'_2\text{U}_2\text{O}_7$ and $\text{M}''\text{U}_2\text{O}_7$. The formulae may also be written $\text{M}'_2\text{UO}_4\cdot\text{UO}_3$ and $\text{M}''\text{UO}_4\cdot\text{UO}_3$.

Barium di-uranate BaU_2O_7 . Formed by ppg. $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2\cdot\text{Aq}$ by $\text{BaO}\cdot\text{Aq}$ (Berzelius, P. 1, 359); also by heating to redness $\text{UO}_2\cdot\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ (Wertheim, J. pr. 29, 207). A yellowish-red powder.

Calcium di-uranate CaU_2O_7 . Formed, according to Ditte (*C. R.* 95, 988), by strongly heating U_3O_8 with $\text{Ca}(\text{ClO}_4)_2$; a yellowish-green solid.

Copper di-uranate CuU_2O_7 . This salt is said to be formed, as a green crystalline powder, by fusing $\text{Cu}(\text{UO}_2\cdot\text{PO}_4)_2\cdot 8\text{aq}$ with Na_2CO_3 , and washing with water (Debray, A. Ch. [8] 61, 451).

Lead di-uranate PbU_2O_7 . Formed by digesting $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2\cdot\text{Aq}$ with freshly pptd. PbCO_3 (Wertheim, J. pr. 29, 207); also by adding NH_4Aq to a mixture of $\text{UO}_2(\text{NO}_3)_2\cdot\text{Aq}$ and $\text{Pb}(\text{NO}_3)_2\cdot\text{Aq}$ (Arfvedson, P. 1, 258). A yellowish-

red powder, becoming green when heated; strongly heated in H, gives a pyrophoric mixture of Pb and UO_2 .

Potassium di-uranate $K_2U_2O_7$. Formed by melting together UO_2 and K_2CO_3 and washing with water; also by strongly heating $UO_2 \cdot K_2(CO_3)_2$ or $UO_2 \cdot K(C_2H_3O_2)_2$ (Berzelius, *P.* 1, 359). A yellowish-red powder.

Silver di-uranate $Ag_2U_2O_7$. Obtained by adding amorphous K_2UO_4 to molten $AgNO_3$, and washing with ice-cold water (Alibegoff, *A.* 232, 129; 233, 117, 143). Also by strongly heating $UO_2 \cdot Ag(C_2H_3O_2)_2$ (Wertheim, *J. pr.* 29, 221; cf. Rammelsberg, *P.* 59, 10). An amorphous, yellow-red solid; easily sol. acids; decomposed by hot water (Alibegoff, *loc.*).

Sodium di-uranate $Na_2U_2O_7$. Gaq. Obtained by ppg. uranyl salts by $NaOH$ aq (Patera, *J. pr.* 51, 125; cf. Stolba, *Fr.* 3, 74). Loses water of crystallisation over H_2SO_4 . A light-yellow to darkish-yellow powder. Known commercially as *uranium yellow* (*v.* DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 893).

Di-uranate of strontium SrU_2O_7 , is said also to exist (Ditte, *C. R.* 95, 988).

TRI-URANATES. The only salt that has been isolated is *sodium tri-uranate* $Na_3U_3O_{10}$; it is prepared by fusing $UO_2(SO_4)$ with $NaCl$, and boiling out with water. This salt forms yellow leaflets resembling mosaic gold; S.G. 6.912; hygroscopic; insol. water, sol. acids (Drenkmann, *J.* 1861. 255).

HEXA-URANATES. The *potassium salt*, $K_6U_6O_{20}$, Gaq., is described as a yellow microscopically crystalline powder, which loses all water at $300^\circ\text{--}400^\circ$; prepared by melting $UO_2(SO_4)$ with KCl (Drenkmann, *J.* 1861. 255).

PER-URANATES. By adding excess of alkali and H_2O_2 aq to solutions of uranyl salts, Fairley (*C. J.* 31, 134) obtained salts which may be formulated as $M_2UO_4 \cdot xaq$ and $M_2U_2O_8 \cdot xaq$ where $M = NH_4, K, \text{ or } Na$, and $R = UO_2$.

Ammonium-uranyl peruranate $(NH_4)_2(UO_2)_3UO_8$. Gaq. The formula may also be written $(NH_4)_2O \cdot UO_2 \cdot O_8$. Gaq., or $(NH_4)_2O \cdot UO_2 \cdot UO_8$. Gaq., or, regarding the compound as a double peroxide of U and NH_4 , as $2UO_2 \cdot (NH_4)_2O_8$. Gaq. The salt is prepared by adding excess of NH_4 aq and H_2O_2 aq to a solution of a uranyl salt and ppg. by alcohol; it is an orange-yellow solid, readily soluble in water. The quantity of $KMnO_4$ in solution decolourised shows that the ratio of U to 'peroxide oxygen' in the salt is U:3O.

Potassium per-uranate $K_2UO_4 \cdot 10aq$. This salt may also be looked on as a double peroxide of U and K ($UO_2 \cdot K_2O \cdot 10aq$), or as $2K_2O \cdot UO_2 \cdot 10aq$. It is prepared by adding alcohol to a solution obtained by treating $UO_2(NO_3)_2$ aq with KOH aq and excess of H_2O_2 aq, and rapidly drying the orange-yellow pp. by pressure in filter paper. The salt rapidly absorbs CO_2 from the air and loses O; it is easily decomposed by heat, giving off H_2O and O. Experiments showed that the ratio of U to 'peroxide oxygen' is U:3O.

Sodium peruranate $Na_2UO_4 \cdot 8aq$. This formula may also be written $UO_2 \cdot Na_2O \cdot 8aq$ or $2Na_2O \cdot UO_2 \cdot 8aq$. The salt is prepared by dissolving 'ordinary uranic hydrate,' or $UO_2 \cdot xaq$, in excess of $NaOH$ aq along with excess of H_2O_2 aq, allowing to crystallise if conc. solutions

are used, or ppg. by a little alcohol if dilute solutions are used, and drying by pressure in filter paper. Poleck (*B.* 27, 1051 [1891]) obtained this salt by adding sodium superoxide to solution of a salt of U. The salt is golden-yellow and lustrous; it slowly absorbs CO_2 from the air, and gives off O. When heated, alone or in CO_2 , it gives off $3O$; it also loses $3O$ in contact with acidified $KMnO_4$ or other unstable O compounds. The ratio of U to 'peroxide oxygen' is U:3O as measured by the quantity of $KMnO_4$ decolourised by a solution of the salt.

Sodium-uranyl per-uranate

$Na_2(UO_2)_3UO_8 \cdot 6aq$. The formula may also be written $Na_2O \cdot UO_2 \cdot UO_8$, Gaq. or $Na_2O \cdot UO_2 \cdot 6aq$; or, regarding the compound as a double peroxide of U and Na, as $2UO_2 \cdot Na_2O \cdot 6aq$. The salt is prepared similarly to $Na_2UO_4 \cdot 8aq$, but using only the minimum quantity of $NaOH$ aq required for solution, and adding alcohol, when it separates as a red oil which slowly crystallises to a red solid. The quantity of $KMnO_4$ in solution decolourised by a solution of the salt showed that the ratio of U to 'peroxide oxygen' is U:3O.

Uranium, oxybromide of, UO_2Br_2 . (*Uranyl bromide*.) In preparing UBr_4 , by heating a mixture of UO_2 and C in Br vapour, Hermann (*J.* 1861. 260) obtained a yellow, easily volatile sublimate, which was probably an oxybromide. By heating UO_2 with Br and $NaCl$, also by dissolving UO_2 in HBr aq, a colourless liquid was obtained, which on evaporation gives yellow needles of the *hydrated oxybromide* $UO_2Br_2 \cdot 7aq$ (Sendtner, *A.* 195, 325). This compound combines with NH_3 and KBr to form $UO_2Br_2 \cdot 2MBr$ (*v.* URANOXYBROMIDES, p. 822).

Uranium, oxychloride of, UO_2Cl_2 . (*Uranyl chloride*.) Formed by strongly heating UO_2 in Cl_2 ; a yellow, crystalline solid, easily fused, but volatilised only at a high temperature; heated with K forms UO_2 and KCl (Peligot, *A. Ch.* [3] 5, 5). By dissolving $UO_2 \cdot H_2O$ in HCl aq, also by oxidising UCl_4 by HNO_3 aq and evaporating, yellowish-green crystals of $UO_2Cl_2 \cdot xH_2O$ are obtained (Klaproth, *Crelt's A.* 1789 [2]. 387).

By dissolving UO_2Cl_2 in ether and evaporating, Regelsberger (*A.* 227, 119) obtained yellow needles of the compound $UO_2Cl_2 \cdot 2Et_2O$.

UO_2Cl_2 forms compounds with NH_3 , Cl and Cl_2 of the form $2MCl \cdot UO_2Cl_2$ (*v.* URANOXYCHLORIDES, p. 823).

UO_2Cl_2 combines with NH_3 to form $UO_2Cl_2 \cdot xNH_3$, where $x = 2, 3, \text{ and } 4$. The first of these compounds, $UO_2Cl_2 \cdot 2NH_3$, is formed by passing dry NH_3 into UO_2Cl_2 dissolved in ether, drying the voluminous yellow pp. that forms, and then placing it *in vacuo* over H_2SO_4 , until all ether is removed; the second compound, $UO_2Cl_2 \cdot 3NH_3$, is formed by the action of NH_3 on $UO_2Cl_2 \cdot 2NH_3$; and a mixture of $UO_2Cl_2 \cdot 3NH_3$ and $UO_2Cl_2 \cdot 4NH_3$ is produced by passing NH_3 over solid UO_2Cl_2 . When strongly heated in air these compounds give off all NH_3 and Cl and leave U_2O_5 ; heated out of contact with air they give UO_2 (Regelsberger, *A.* 227, 119). The three compounds are called by B. *uranyl ammonium chlorides*, and their formulae are written $UO_2(NH_4Cl)_2$, $UO_2(NH_4Cl)(NH_4NH_2Cl)$, and $UO_2(NH_4NH_2Cl)_2$. Water reacts thus:—
(1) $3UO_2(NH_4Cl)_2 + 3H_2O = (NH_4)_2U_2O_7 + UO_2Cl_2 + 4NH_4Cl$

(2) $\text{UO}_2(\text{NH}_4\text{Cl})_2 + 2\text{H}_2\text{O} = \text{UO}_2(\text{OH})_2 + 2\text{NH}_4\text{Cl}$; the second reaction takes place quickly with warm water.

Uranium oxyfluoride of, UO_2F_2 . (Uranyl fluoride.) This compound is produced by boiling U_3O_8 with HFAq , filtering off UF_3 (v. URANIUM TETRAFLUORIDE, p. 823), and evaporating the filtrate; it is also formed, in small quantities, by heating UF_4 in a closed Pt crucible. The compound differs according to the method of preparation (Smithells, *C. J.* 43, 125).

α -Oxyfluoride. About 1 gram UF_4 is heated in a Pt crucible with the lid on, temperature being raised as quickly as possible; after five minutes the crucible is allowed to cool, the light, bulky sublimate is removed, and the crucible is again heated for five minutes, and these processes are repeated several times (S., *l.c.* p. 129). This form of UO_2F_2 is a very bulky, light, white, crystalline solid; it is very soluble in water, forming a yellow liquid; heated in air it is gradually changed to U_3O_8 .

β -Oxyfluoride. U_3O_8 is treated with boiling HFAq in a leaden vessel, the yellow solution is poured off from green UF_3 , heated until the excess of HF is driven off, and allowed to evaporate; evaporation may be completed over H_2SO_4 and CaO *in vacuo*; the residue is dried at 100° (S., *l.c.* p. 130). This form of UO_2F_2 is a yellow saponaceous mass; in one instance the preparation had a semi-crystalline appearance, forming yellow, lustrous scales; it is very soluble in water or alcohol; heated on Pt foil U_3O_8 is formed; heated in a closed crucible it is slowly decomposed, giving UO_2 . β - UO_2F_2 probably forms a compound with HF , by evaporating a solution of U_3O_8 in HFAq over H_2SO_4 and CaO until the weight was constant, Smithells (*l.c.* p. 131) obtained a substance which gave results on analyses agreeing fairly with the formula $\text{UO}_2\text{F}_2 \cdot \text{HF} \cdot \text{H}_2\text{O}$.

A solution in water of either form of UO_2F_2 mixed with KFAq and KHF_4aq , and evaporated, gives the quadric acid fluoxy-urate $\text{K}_4\text{UO}_2\text{F}_6$ (S., *l.c.* p. 130-1). For the compounds of UO_2F_2 with MF v. URANOXYFLUORIDES (p. 824).

Ditte (*C. R.* 91, 115) gave the formula UOF_2 to the sublimate obtained by heating, in a closed Pt crucible, the solid that remained when U_3O_8 was treated with boiling HFAq . Ditte said that this solid was UO_2F_2 ; Smithells (*l.c.*) has, however, shown that the solid obtained by the method used by Ditte is UF_4 , and that the sublimate formed by heating this is α - UO_2F_2 .

Uranium oxysulphides of. Two compounds probably exist.

URANIUM OXYSULPHIDE $\text{U}_3\text{O}_2\text{S}_2$. This composition was given by Hermann (*J.* 1861, 258) to a dark, greyish-black solid, obtained by heating UO_2 , U_3O_8 , or NH_4 uranate to redness in vapour of CS_2 . Dissolves in conc. HClAq ; burns when heated in air (cf. H. Rose, *G. A.* 73, 139).

URANYL SULPHIDE $(\text{UO}_2)_2\text{S}$. A brown solid, obtained by prep. an ammoniacal solution of a uranyl salt by cold $(\text{NH}_4)_2\text{SAq}$, and quickly washing with conc. alcohol. Probably not obtained pure, as it quickly decomposes; water produces $\text{UO}_2 \cdot \text{H}_2\text{O}$; at 40° – 50° it is changed to UO_2 and S (Remelé, *P.* 124, 114; Zimmermann, *A.* 204, 204). $(\text{UO}_2)_2\text{S}$ is somewhat sol. water or dilute alcohol; dissolved by conc. HClAq , giving UCl_4

and S; dissolved by $(\text{NH}_4)_2\text{SAq}$, only in presence of $(\text{NH}_4)_2\text{CO}_3\text{Aq}$ (Zimmermann, *l.c.*), forming a brown liquid.

Uranium black. By allowing $(\text{UO}_2)_2\text{S}$ to stand in contact with freshly prepared $(\text{NH}_4)_2\text{SAq}$, in absence of air, a dull black amorphous powder is obtained. This solid dissolves in mineral acids, giving off traces of H_2S ; it dissolves partly in warm $(\text{NH}_4)_2\text{CO}_3\text{Aq}$, but not in warm $(\text{NH}_4)_2\text{SAq}$, nor in caustic alkali solutions; heated in a tube to c. 270° it gives off a very little NH_3 and H_2O . Zimmermann (*A.* 204, 204) gives the formula U_3O_8 to uranium black, neglecting (as impurities) the traces of NH_3 and S which the substance contains.

Uranium red. By allowing $(\text{UO}_2)_2\text{S}$ to stand for 24–48 hours in contact with cold $(\text{NH}_4)_2\text{SAq}$, exposed to air, a deep-red solid is obtained; soluble in dilute mineral acids, with separation of S and evolution of H_2S ; gives off NH_3 , S, and H_2O when heated to 150° and, at above 200° , leaves U_3O_8 (Zimmermann, *l.c.*). According to Z., the formation of this red substance takes place only when $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is present in the $(\text{NH}_4)_2\text{SAq}$ used; $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is formed by the action of the air. Z. gives to uranium red the composition $\text{U}_2\text{S}(\text{NH}_4)_2\text{O}_2 = \text{UO}_2 \cdot \text{ONH}_4 \cdot \text{SNH}_4 \cdot 2\text{UO}_2$ (cf. Patern, *J. pr.* 51, 122; Remelé, *P.* 124, 165; Hermann, *J.* 1861, 14).

Uranium, salts of. Two classes of salts are formed by treating oxides of U with acids; UO_2 forms corresponding salts, UX , when X = the radicle of a dibasic acid, and UX , when X = the radicle of a monobasic acid; UO_3 forms salts $(\text{UO}_3)_\text{X}$ when X = the radicle of a dibasic acid, and $(\text{UO}_3)_\text{X}$, when X = the radicle of a monobasic acid. The salts UX^I and UX^{II} are called *uranous salts*; and $(\text{UO}_3)_\text{X}^I$ and $(\text{UO}_3)_\text{X}^{II}$ are called *uranyl salts*. (For reactions of the two classes of salts v. URANIUM, *Detection and estimation of*, p. 822.) Besides the normal salts, a large number of basic salts of both classes is known, and also many double salts.

The chief *uranous salts* are *arsenates*, *phosphates*, and *sulphites*. The chief *uranyl salts* are *arsenates*, *bromate*, *double carbonates*, *chromates*, *hypophosphite*, *iodate*, *nitrate*, *oxalate*, *phosphates*, *phosphite*, *selenates*, *selenites*, *sulphates*, and *sulphites* (v. NITRATES, SULPHATES, &c.).

Uranium, sulphides of. When U is burnt in vapour of S, the disulphide US_2 is formed; by passing H_2S over heated UBr_3 the sesquisulphide U_2S_3 is produced; and by heating U_3S_8 in H the monosulphide US is obtained. The mol. w. of none of these is known.

URANIUM DISULPHIDE US_2 . Prepared by heating U in vapour of S (Péligot, *P.* 54, 422; cf. Zimmermann, *A.* 216, 18); also by heating UCl_4 to redness in H_2S (Hermann, *J.* 1861, 258). A dark greyish-black powder; becomes crystalline when fused with borax; oxidises slowly in air, rapidly on heating. Easily soluble in conc. HClAq (Hermann, *l.c.*).

URANIUM SESQUISULPHIDE U_2S_3 . A stream of dry H_2S , perfectly free from air, is passed over heated UBr_3 , as long as HBr is given off. Grey-black solid, forming pseudomorphs of UBr_3 ; decomposes in air, giving off H_2S ; burns when heated in air; scarcely acted on by HClAq or

dilute HNO_3 ; decomposed violently by conc. HNO_3 (Alibegoff, A. 233, 117).

URANIUM MONOSULPHIDE US . A black, amorphous powder; obtained by passing dry H over U_2S_3 kept at a red heat, for c. 40 hours, until H_2S is no longer given off. Similar in properties to U_2S_3 (Alibegoff, A. 233, 135).

URANIUM THIO-ACIDS, salts of. No thio-acid, nor salt of a thio-acid, of U has been definitely isolated. *Uranium red* (v. supra, p. 828) may perhaps be an ammonium oxythionate of U .

M. M. P. M.

URANOXYBROMIDES v. p. 822, under

URANIUM TETRABROMIDE.

URANOXYCHLORIDES v. p. 823, under

URANIUM TETRACHLORIDE.

URANOXYFLUORIDES v. p. 824, under

URANIUM TETRAFLUORIDE.

URANYL COMPOUNDS, compounds of the radicle UO_2 ; v. **URANYL AMMONIUM CHLORIDES** (p. 827), **URANYL BROMIDE** (p. 827), **URANYL FLUORIDE** (p. 828), **URANYL SALTS** (p. 828), **URANYL SULPHIDE** (p. 828).

URAZOLE. A name given by Pinner (B. 20, 2358) to di-oxy-triazole, which may be represented as $\text{NH}_2\text{C}(\text{OH})=\text{N}$ or $\text{NH}_2\text{CO}=\text{NH}$.

UREA $\text{CH}_4\text{N}_2\text{O}$, i.e. $\text{CO}(\text{NH}_2)_2$. *Carbamide*. Mol. w. 60. [152.] (Lubavin, B. 3, 205). S.G. 1.323 (Schröder, B. 12, 562). S. (alcohol) 20 in the cold; 100 at 78° . H.C.v. 152,500. H.C.p. 152,200 (Stohmann & Langbein, J. pr. [2] 44, 387); 160,900 (Berthelot & Petit, C. R. 109, 759; 110, 887). H.F. 80,800.

Occurrence.—In the urine of mammalia, especially in that of flesh-eaters (Fourcroy & Vauquelin, A. D. 1799). Occurs in small quantity in blood, muscle, chyle, and lymph of mammalia (Wurtz, C. R. 49, 52; Poisseuille & Gobley, J. 1859, 612; Verdelin & Dollfus, A. 74, 214; Munk, Pf. 11, 100; Pickard, C. R. 83, 1179; 87, 533; Gréhan & Quinquand, C. R. 108, 1092; Garrod, Pr. 53, 478). Constitutes about 30 p.c. of the solid substance of the vitreous humour of the eye (Millon, C. R. 26, 119; A. 66, 128). Occurs also in saliva (Rabuteau, J. 1873, 877), in cow's milk (Lefort, Z. 1866, 190; Vogel, J. 1867, 932), and in other animal secretions.

Formation.—1. By evaporating a solution of ammonium cyanate (Liebig & Wöhler [1828], B. J. 12, 266; P. 12, 253; 15, 619; A. 38, 108). 2. By adding a little HNO_3 to an ethereal solution of cyanamide (Cannizzaro & Cloëz, A. 78, 230) or by the action of dilute (50 p.c.) H_2SO_4 on cyanamide (Baumann, B. 6, 1373).—3. From COCl_2 and dry NH_3 (Regnault, A. Ch. [2] 69, 180; Natanson, A. 98, 287), guanidine and NH_4Cl being formed at the same time (Fenton, C. 7, 35, 793).—4. By heating carbonic ether, with NH_4Aq at 180° .—5. By heating ammonium carbamate at 140° (Basaroff, J. pr. [2] 1, 283).—6. By passing an alternating electric current through a solution of ammonium carbamate (Drechsel, J. pr. [2] 22, 481).—7. By electrolysis of ammonia solution, using carbon electrodes (Milot, B. [2] 46, 243).—8. By passing a mixture of NH_3 and CO_2 through a red-hot tube (Dexter, Am. 4, 85).—9. Formed by passing air charged with NH_3 and vapour of benzene over a red-hot helix of platinum wire (Herroun, C. J.

89, 471). Acetylene, but not ethylene, may be substituted for benzene.—10. By heating ammonium thiocarbamate $\text{NH}_4\text{CO}_2\text{SNH}_2$, or by shaking it with water and PbCO_3 .—11. By the action of aqueous KMnO_4 on thio-urea (Maly, M. 11, 277).—12. By the action of KMnO_4 on KC_2N in acid solution (Baudrimont, J. 1880, 393).—13. By the action of NH_4Aq and H_2S on copper fulminate (Gladstone, A. 66, 2).—14. By heating oxamide with HgO (Williamson, Mémoires du Congrès scientif. de l'Europe, A.D. 1847).—15. By oxidation of uric acid.—16. By the action of KClO_4 and HCl on guanine (Strecker, A. 118, 159).—17. By boiling guanidine with baryta (Baumann, B. 6, 1370).—18. By boiling biguanide sulphate or phenyl-biguanide sulphate with baryta (Emich, M. 12, 11).—19. By the action of baryta on arginin (Schulze & Likiernik, B. 24, 2701).—20. By boiling creatin with baryta.—21. A product of oxidation of proteins by KMnO_4 (Béchamp, A. Ch. [3] 48, 348; C. R. 70, 866; Ritter, B. [2] 16, 327). Stædeler (J. pr. 72, 251) and Loew (J. pr. [2] 2, 289) failed to obtain urea in this manner. Dreschel (B. 23, 3097) obtained urea from albumen by electrolysis, but not by oxidation.

Preparation.—1. Urine, concentrated by evaporation, is treated with nitric or oxalic acid, and the ppl. nitrate or oxalate of urea is decomposed by CaCO_3 .—2. A solution of potassium cyanate mixed with ammonium sulphate is evaporated on a water-bath to dryness, and the residue extracted with alcohol.—3. A mixture of dry K_2FeCy_4 (28 pts.) and MnO_2 (14 pts.) is heated till sticky on an iron plate. A cold aqueous extract of the mass is mixed with $(\text{NH}_4)_2\text{SO}_4$ (20.5 pts.), evaporated to dryness, and extracted with alcohol (Liebig).—4. Dry K_2FeCy_4 (8 pts.) is fused with K_2CO_3 (3 pts.) and PbO (15 pts.) added to the melted mass. The cooled mixture is dissolved in water, mixed with $(\text{NH}_4)_2\text{SO}_4$ (8 pts.) evaporated, and extracted with alcohol (Clemm, A. 66, 382). Any K_2FeCy_4 left can be removed by FeSO_4 .—5. Lead cyanate is digested with $(\text{NH}_4)_2\text{SO}_4$ (J. Williams, C. J. 21, 64).—6. From NH_4Aq , CO_2 , and lead carbonate (Schmidt, B. 10, 193).—7. By the action of $(\text{NH}_4)_2\text{SO}_4$ on KC_2O obtained by heating dry K_2FeCy_4 with $\text{K}_2\text{Cr}_2\text{O}_7$; the yield being 25 p.c. of the weight of ferrocyanide (O. A. Bell, C. N. 32, 99).—8. A stream of dry NH_3 gas is passed through phenyl-carbonate (from phenol-sodium and COCl_2), melted in a water-bath, and the melt is then poured into hot water; the aqueous solution after separation from the phenol is evaporated to crystallisation (Hentschel, B. 17, 2286).

Properties.—Dimetric crystals, v. a. sol. water, y. sol. cold alcohol, insol. CHCl_3 , nearly insol. ether. Sublimes at 130° . In *vacuo* it distils at 135° (Bourgeois, B. [3] 7, 48). Urea is not attacked by pure HNO_3 (Franchimont, R. T. C. 6, 217).

Reactions.—1. When heated alone at 150° – 170° it yields NH_3 , cyanuric acid and biuret; at 140° it yields ammelide.—2. Decomposed into CO_2 and NH_3 by heating with water in sealed tubes above 100° , by boiling with potash, lime, or magnesia, by warming with conc. H_2SO_4 , by evaporating with lead acetate, and by the action of ozone (Gorup-Besanez, A. 125, 207).

in presence of free alkali. CaO produces cyanamide (Emich, *M.* 10, 330). A 8 p.c. HCl solution decomposes 4 p.c. of the urea in 24 hours. NaOHAq of the same strength has less effect. Cold water does not decompose urea (Berthelot & André, *Bl.* [2] 47, 840).—3. *Alcoholic potash* forms, on heating in sealed tubes, cyanic acid, NH_3 , and water (Haller, *Bl.* [2] 45, 705).—4. Urea hydrochloride at 145° yields NH_4Cl and cyanuric acid (De Vry, *A.* 61, 249).—5. *Chlorine* passed over melted urea forms HCl, nitrogen, NH_4Cl , and cyanuric acid (Wurtz, *A.* 64, 307).—6. *Hypochlorous acid, hypochlorites, chlorine-water, and hypochlorites*, set free nitrogen, e.g. $\text{CON}_2\text{H}_4 + 3\text{HOCl} = \text{CO}_2 + 3\text{HCl} + 2\text{H}_2\text{O} + \text{N}_2$.—7. *Nitrous acid* added to a hot solution forms CO_2 and nitrogen: $\text{CON}_2\text{H}_4 + \text{N}_2\text{O}_3 = \text{CO}_2 + 2\text{H}_2\text{O} + 2\text{N}_2$. Nitrous acid (2 mols.) when added to a cold solution of urea (1 mol.) reacts as follows: $2\text{CON}_2\text{H}_4 + \text{N}_2\text{O}_3 = (\text{NH}_4)_2\text{CO}_3 + 2\text{N}_2 + \text{CO}_2$ (Claus, *B.* 4, 140).—8. Neutral KMnO_4 has no action in the cold, and acts but slowly at 100° . In acid solutions KMnO_4 gives off nitrogen (1 vol.) and CO_2 (2 vols.) (Béchamp, *J.* 1856, 696; cf. Wanklyn & Gamgee, *C. J.* 21, 25).—9. *Bromine* added gradually to an alcoholic solution of urea forms NH_4Br , cyanuric acid, and nitrogen. In sealed tubes Br gives NH_4Br and cyanamide (Smolka, *M.* 8, 64).—10. Heating with P_2O_5 forms cyanic and cyanuric acids, ammeline, cyanamide, and NH_3 (Weltzien, *A.* 107, 219).—11. Yields cyanamide on warming with Na (Fenton, *C. J.* 41, 262).—12. Conc. HNO_3 reacts thus: $\text{CON}_2\text{H}_4 + 2\text{HNO}_3 = \text{CO}_2 + \text{N}_2\text{O} + \text{NH}_4\text{NO}_3 + \text{H}_2\text{O}$ (Franchimont, *R. T. C.* 2, 96; 3, 219).—13. P_2S_5 forms crystalline $\text{C}_2\text{H}_4\text{N}_4\text{P}_2\text{S}_5\text{O}_2$, which yields $\text{C}_2\text{H}_4\text{AgN}_4\text{P}_2\text{S}_5\text{O}_2$ and $\text{C}_2\text{H}_4\text{Ag}_2\text{N}_4\text{P}_2\text{S}_5\text{O}_2$, and gives off PH_3 on warming (Kutschig, *M.* 9, 406).—14. *Zinc dust* at a red heat forms ZnCy_2 , ammonia, and hydrogen (Aufschlager, *M.* 13, 272).—15. CS_2 at 100° forms COS and ammonium sulphocyanide. With alcohol and CS_2 the products are mercaptan, CO_2 , and ammonium sulphocyanide (Ludenburg, *Z.* [2] 5, 253; *B.* 1, 273; 2, 271; Fleury, *A.* 123, 144).—16. *Alcohols* in sealed tubes form carbamic ethers and alkylallophanates (Cahours, *C. R.* 76, 1387).—17. Boiling Ac_2O forms acetamide and diacetamide (Hofmann, *B.* 14, 2733).—18. ZnEt_2 forms $\text{CON}_2\text{H}_4\text{Zn}$, which is reconverted into urea by water (Gal, *Bl.* [2] 39, 648).—19. *Oxalic ether* at 135° – 170° forms oxamide, allophanic ether, and alcohol (Grabowski, *A.* 134, 115). *Oxamic ether* forms, on fusion, oxalamide (Carstanjen, *J. pr.* [9] 9, 143).—20. *Methylamido-acetic acid* (sarcosine) forms methyl-hydantoin on fusion (Ruppert, *B.* 6, 1278).—21. *Aniline* at 150° gives NH_3 and di-phenyl-urea (Baeyer, *A.* 131, 251).—22. *Aniline sulphonic acid* at 120° gives NH_3 , CO , $\text{NH}_4\text{C}_6\text{H}_4\text{SO}_3\text{H}$ (Vilbo, *Bl.* [5] 6, 6).—23. *Biguanide sulphate* forms, on heating, ammeline, NH_3 , and $(\text{NH}_4)_2\text{SO}_4$ (Smolka & Friedreich, *M.* 10, 95).—24. Heated with acetone and ZnCl_2 or P_2O_5 at 110° – 140° it gives *s-tri-methylpyridine* and base $\text{C}_4\text{H}_8\text{N}$ [119°]; (320°) (Riehm, *A.* 238, 22). This base forms hard monoclinic crystals, with metallic ring; its solutions fluoresce. It gives $\text{B}_2\text{H}_6\text{PtCl}_6$: [225°].—25. Heated with *acetyl-acetone* (1 mol.), urea (2 mols.) forms $\text{CH}_3\text{C}(\text{Me})\text{N}:\text{CO}:\text{NH}_2$, which crystallises from alcohol [200°] (Combes, *Bl.* [3]

7, 790). The same body is formed, together with $\text{CH}_3\text{C}(\text{Me})\text{N}:\text{CO}$ [198°], by adding HClAq or H_2SO_4 to an alcoholic solution of urea and acetyl-acetone (Evans, *J. pr.* [2] 46, 352; 48, 499).—26. *Benzoyl-acetone* forms, in like manner, $\text{Bz}:\text{CH}_2\text{C}(\text{Me})\text{N}:\text{CO}:\text{NH}_2$ [191°] and $\text{CH}_3\text{C}(\text{Me})\text{N}:\text{CO}$ [227°] (Evans, *J. pr.* [2] 46, 352; 48, 509).—27. *Acetoacetic ether* (2 mols.) and NaOEt (2 mols.) form in the cold $\text{C}_{12}\text{H}_{22}\text{N}_4\text{O}_2\text{Na}_2$ [c. 165°] (Ernert, *A.* 258, 361). Acetoacetic ether in alcoholic solution forms uranido-crotonic acid (*q. v.*).—28. Urea reacts with aldehydes in the cold. In aqueous solution a diureide $\text{R}:\text{CH}(\text{NH}:\text{CO}:\text{NH}_2)_2$ is usually formed, while solid urea forms triureides. On warming with excess of aldehyde, di- and tri-ureides yield tetra- and hexa-ureides (H. Schiff, *A.* 151, 186). These ureides are sparingly soluble neutral solids, and are split up by warming with acids into the parent substances. Benzoic aldehyde forms benzylidene-di-urea (*q. v.*), while *o*-oxy-benzoic aldehyde forms $\text{C}_6\text{H}_4(\text{OH})\text{CH}(\text{NH}:\text{CO}:\text{NH}_2)_2$ aq, which is converted by acetoacetic ether in alcohol into $\text{C}_6\text{H}_4(\text{OH})\text{CH}:\text{N}:\text{CO}:\text{N}:\text{C}(\text{Me})\text{CH}:\text{CO}_2\text{Et}$ [200°], $\text{C}_6\text{H}_4(\text{OH})\text{CH}:\text{N}:\text{CO}:\text{NH}:\text{C}(\text{Me})\text{CH}:\text{CO}_2\text{Et}$ [204°], and $\text{C}_6\text{H}_4\text{CH}:\text{N}:\text{CO}:\text{NH}:\text{C}(\text{Me})\text{CH}:\text{CO}_2\text{Et}$ [204°], and $\text{C}_6\text{H}_4\text{CH}:\text{N}:\text{CO}:\text{NH}:\text{C}(\text{Me})\text{CH}:\text{CO}_2\text{Et}$ [204°], which decomposes between 260° and 270° (Biginelli, *B.* 24, 2963). Acrolein forms $(\text{CON}_2\text{H}_4)_3\text{C}_2\text{H}_3\text{O}$, which chars at 250° (Lüdy, *M.* 10, 295). *o*-Nitrobenzoic aldehyde forms nitro-benzylidene-di-urea $\text{C}_6\text{H}_4(\text{NO}_2)\text{CH}(\text{NH}:\text{CO}:\text{NH}_2)_2$ aq [190°]. In like manner cumic aldehyde in alcohol forms the di-ureide $\text{C}_6\text{H}_5\text{CH}(\text{NH}:\text{CO}:\text{NH}_2)_2$ [176°] (Biginelli, *B.* 24, 2964), and cinnamic aldehyde forms $\text{Ph}:\text{CH}:\text{CH}:\text{CH}(\text{NH}:\text{CO}:\text{NH}_2)_2$ [172°], and compounds melting at 116° and 212° .—29. *Chloral* added to conc. aqueous solutions of urea forms $(\text{C}_2\text{HCl}_3\text{O})\text{CON}_2\text{H}_4$ [150°], v. e. sol. hot water, and $(\text{C}_2\text{HCl}_3\text{O})\text{CON}_2\text{H}_4$ [190°] nearly insol. hot water, both compounds being crystalline (Jacobsen, *A.* 157, 246). Chloral cyanhydrin at 105° forms the very stable crystalline $\text{C}_2\text{H}_4\text{Cl}_2\text{N}_4\text{O}$ (Pinner & Fuchs, *B.* 10, 1069).—30. *Benzene sulphonic chloride* at 100° forms colourless crystals of $\text{C}_6\text{H}_5\text{SONH}_2\text{C}_6\text{H}_4\text{SO}_3\text{H}$ (Elander, *Bl.* [2] 34, 207). Naphthalene (*a*)-sulphonic chloride acts similarly.—31. *Cinnamoyl chloride* forms $\text{C}_6\text{H}_5(\text{NH}:\text{CO}:\text{NH}:\text{C}_6\text{H}_4\text{SO}_3\text{H})_2$ [184°] (Biginelli, *B.* 24, 2965).—32. ClCH_2OH forms methylene-urea, which is split up by hot dilute H_2SO_4 into formic aldehyde and urea (Von Hemmelmayr, *M.* 12, 89).—33. *Trichlorolactic acid* and a little water form, on heating, acetylene-urea $\text{C}_2\text{H}_2\text{N}_4\text{O}_2$ (Pinner, *B.* 17, 1997).—34. *Hexachloro-acetone* (2 mols.) heated with urea (1 mol.) at 150° forms $\text{CO}:\text{N}_2\text{H}_4\text{C}(\text{Cl})_2\text{O}$, crystallising from alcohol in hexagonal plates (Cloëz, *A. Ch.* [6] 9, 145).

Detection.—Urea gives, in conc. solution, crystalline pps. with nitric and oxalic acids. Urea dissolved in amyl alcohol is completely pptd. by an ethereal solution of oxalic acid (Brücke, *M.* 3, 195). Murexide (*C. R.* 78, 182) filters out of urine, dries the filter at 35° , and employs it as a test for urea, which it converts into ammonium carbonate. A conc. aqueous solution of furfuraldehyde followed by a drop of HClAq (S.G. 1.10) colours a crystal of urea

violet (Schiff, *B.* 10, 774). *o*-Nitro-benzoic aldehyde added to an alcoholic solution of urea forms, on warming, a white pp. of *o*-nitro-benzylidene-di-urea [200°]. When present in small quantities this compound may be detected by resolving into the parent substances by boiling with very dilute H_2SO_4 , and then adding a little phenylhydrazine solution, which produces a red colour (Lüdy, *M.* 10, 295). Mercuric nitrate gives a white pp. with solutions of urea. The various methods of estimating urea may also be employed for its detection.

Estimation. — Hypobromite method. Urea is mixed with NaOH (100 g. in 250 c.c. water) to which bromine (25 g.) has been added, and the nitrogen collected and measured (Knop, *Fr.* 9, 226; Hüfner, *J. pr.* [2] 3, 1; Dupré, *C. J.* 31, 534; Simpson a. Keefe, *C. J.* 31, 838; Russell a. West, *C. J.* 27, 749; Eykman, *R. T. C.* 3, 125; Schleich, *J. pr.* [2] 10, 263; Colquhoun, *C. N.* 67, 123; Camerer, *Zeit. Biol.* 29, 239). When this method is applied to urine it must be remembered that uric acid gives off 48 p.c. and creatinin 37 p.c. of its nitrogen in this way (Falk, *Fr.* 21, 300). Nevertheless, the quantity of nitrogen evolved is 8 p.c. less than the calculated amount (R. a. W.). Using Knop's solution, ammonia, urea, and oxamide give off 93, 92.3, and 75 p.c. of their nitrogen as gas (Foster, *C. J.* 33, 470; 35, 129). In the case of urea and oxamide the 'suppressed' nitrogen is present as cyanate and as nitrate (Fauconier; Luther, *H.* 13, 500). The amount of 'suppressed' nitrogen is less in dilute than in concentrated solutions (Hüfner, *H.* 1, 350; cf. Pflüger a. Bohlend, *Pf.* 38, 325; 39, 1, 143), and is greatly diminished by the addition of 1 to 5 p.c. acetoacetic ether (Jacoby, *Fr.* 24, 318). According to Duggan (*Am.* 4, 47), if bromine is added to a solution of urea in NaOHaq the yield of nitrogen is 99.4 p.c. of the theoretical amount. In estimating urea in urine Pflüger (*Fr.* 26, 117) adds HClAq (1 c.c.) to urine (10 c.c.), ppts. various nitrogenous bodies by phosphotungstic acid, neutralises the filtrate with lime and then adds an equal volume of conc. NaOHaq and, after allowing to stand for some time, decomposes with Knop's hypobromite. Frothing of albuminous urine can be avoided by first shaking with a pilule of fat (Méhu, *J. Ph.* [5] 15, 607). Hamburger (*R. T. C.* 2, 181) introduced a volumetric method of employing hypobromite, but Pflüger a. Schenck (*Pf.* 37, 899) consider the method to be untrustworthy. E. Salkowski adds two drops of HCl to urine (2.5 c.c.) diluted with 5 or 10 volumes of water until the air is expelled from the flask, then adds the hypobromite, continues boiling, and collects the nitrogen. Fenton (*C. J.* 33, 300) recommends the use of sodium hypochlorite, which was first proposed by E. W. Davy (A.D. 1854). In this case free $NaOH$ must not be present, though excess of Na_2CO_3 may be present.

Mercuric nitrate method. Urea is completely pptd. by a solution of $Hg(NO_3)_2$. The white pp. is not decomposed, and therefore not turned yellow by Na_2CO_3 . Urine (2 vols.) is mixed with a solution (1 vol.) prepared from saturated solutions of baryta (2 vols.) and $Ba(NO_3)_2$ (1 vol.); filtered through a dry filter

from the ppd. sulphate and phosphate and 15 c.c. (equivalent to 10 c.c. urine) of the filtrate are titrated with standard mercuric nitrate till a drop taken out gives a yellow pp. with Na_2CO_3 (Liebig, *A.* 85, 370). Assuming the compound CON_2H_2HgO to be formed, 1 pt. urea should ppt. 7.2 pts. HgO , but in practice 7.72 pts. of the latter are required. A solution of 71.48 g. mercury in HNO_3 diluted to 1 litre is equivalent to .01 g. urea per c.c. If the urine contains more than 2 p.c. urea the titration gives too low results; in this case the urine must be diluted. When mercuric nitrate is added to a solution of urea nitric acid is set free. Liebig recommended the addition of Na_2CO_3 from time to time to keep the liquid neutral. Pflüger (*Fr.* 19, 375) proceeds as follows: During the titration, after each addition of $Hg(NO_3)_2$ a drop is placed in contact with a little pasty $NaHCO_3$. Long before the titration is ended, a yellow colour is seen between the two drops, but disappears on mixing them together. When the yellow colour is permanent, the titration is near its end; at this point the solution is neutralised by Na_2CO_3 , and the titration continued till a permanent yellow colour is got on mixing the drops. Should the entire liquid become yellow on adding Na_2CO_3 , a fresh quantity of urea solution must be taken and the operation repeated with greater speed. The presence of over 1 p.c. NaCl in urine interferes with the titration when Na_2CO_3 is used as indicator, the final reaction not being sharp. Since $NaHCO_3$ does not ppt. $HgCl_2$, when the bicarbonate is used as indicator the titration may proceed as if NaCl were absent, subtracting the amount of $Hg(NO_3)_2$ that is converted into $HgCl_2$ by the chloride (Rautenburff, *A.* 133, 55; Pfeiffer, *Fr.* 24, 475; Pflüger, *Fr.* 27, 120). It is, however, better to ppt. the chlorides by $AgNO_3$ and titrate in the usual way.

Barium carbonate method. The solution is heated with $BaCl_2$ and NH_4Aq in sealed tubes at 220°-240° and the ppd. $BaCO_3$ weighed (Lunsen, *A.* 65, 575). Before applying this method to urine other substances which might form $BaCO_3$ must be pptd. by phosphotungstic acid (Pflüger a. Bleibtreu, *Fr.* 28, 377).

Kjeldahl's method. Nitrogen in urea may be estimated by Kjeldahl's method. 5 c.c. urine are heated with H_2SO_4 (10 c.c.), and Nordhausen H_2SO_4 (10 c.c.) until no more water or gas comes off, and the liquid is clear yellow. After cooling, water (200 c.c.) and $NaOH$ are added and NH_3 distilled off. In the case of urine it must be remembered that about 13 p.p. of the nitrogen is, on an average, combined in substances other than urea (Pflüger, *Pf.* 35, 464; 40, 533; Camerer, *Z. B.* 24, 306).

Other methods. Urea may also be estimated by fermentation and determination of ammonia set free (Miguel, *C. R.* 111, 501).

Canpani (*G.* 17, 137) proposes to decompose urea by nitrous acid, and pass the CO_2 into a solution of lime-water of known strength, and titrate with oxalic acid.

Cazeneuve and Hugouneng (*Bl.* [2] 43, 82) heat urea with a large excess of water and titrate the resulting ammonium carbonate.

Riegler (*F.* 83, 49) decomposes urea with Millon's reagent and measures the mixture of N and CO_2 evolved.

Möbner & Sjöqvist (*Jr.* 80, 888) add 5 c.c. of a saturated solution of BaCl₂ containing 5 p.c. baryta to 5 c.c. urine and then add 100 c.c. of a mixture of 97 p.c. alcohol (2 pts.) and ether (1 pt.). After 24 hours the liquid is filtered, the pp. washed with 50 c.c. alcohol-ether, and the filtrate and washings evaporated at 50° to 25 c.c., MgO and some water added, and the evaporation continued as long as NH₃ comes off. The urea is then determined by Bunsen or Kjeldahl's method (Böttker, *H.* 17, 140f).

Salts.—B'HCl. Very deliquescent crystalline mass, formed from urea and dry HCl. Decomposed by water into urea and HCl. At 140° it yields NH₃Cl and cyanuric acid.—B'HNO₃. Small plates, sl. sol. water and alcohol, v. sl. sol. HNO₃.—B'₂ILC₂O₄. S. 4.4 at 15°. S. (alcohol of S.G. 833) 1.65. Monoclinic tables; *a:b:c* = 1:0.94:4.91; α = 82° 10' (Loschmidt, *Sitz.* W. 51, ii. 7, 384). V. sol. hot water. Ppd. from its aqueous solution by oxalic acid.—B'₂H₂C₂O₄.aq (Lubavin, *A. Suppl.* 8, 83).—B'HAuCl₄.aq: orange-red prisms or needles, v. sol. water, alcohol, and ether.—B'HAuCl₄: yellow needles, v. sol. hot water (Heintz, *A.* 202, 264).—B'₂H₂PtCl₂.aq. Yellow, deliquescent tables, v. sol. water and alcohol, insol. ether (Heintz, *A.* 198, 91).—B'₂H₂PO₄. Large crystals, v. sol. water and alcohol, sl. sol. ether (Lehmann, *Buchn. Rep.* 15, 224; Schneltzer & Birnbaum, *Z.* [2] 5, 206). Its solution does not ppt. MgSO₄.—B'₂2H₂PO₄. Its aqueous solution gives a crystalline pp. of cyanuric acid on heating.

Tri-chloro-acetate B'₂C₂HClO₃. Plates (from alcohol) (De Clermont, *J.* 1873, 536).—**The fumarate** B'₂C₂H₂O₄, maleates B'₂C₂H₂O₄, and B'₂C₂H₂O₄, malate B'₂C₂H₂O₄, gallate B'₂C₂H₂O₄, and succinate B'₂C₂H₂O₄ [145°], all crystallise in monoclinic forms (Loschmidt, *Sitz.* W. 52, ii. 238). The parabanate B'₂C₂H₂N₂O₄ and tartrate B'₂C₂H₂O₄ are trimetric.—The citrate B'₂C₂H₂O₄ is triclinic (L.). An acid tartrate B'₂C₂H₂O₄ and an acid citrate B'₂C₂H₂O₄ have been prepared (Hasiwetz, *J.* 1856, 698).—**Cyanurate** B'₂C₂N₂H₂O₄. Monoclinic crystals.—**Picrate** B'₂C₂H₂N₂O₄ [142°] (Smolka, *M.* 6, 920). S. 1.9 at 18.5°. S. (95 p.c. alcohol) 3 at 18°. Slender yellow needles (from alcohol). **Tri-chloro-methano sulphinate** B'CCl₃SO₂H. [96°–100°]. Thin prisms (McGowan, *J. pr.* [2] 34, 220).

Compounds with metallic oxides.—B'₂Ag₂O (Liebig). Formed by adding moist Ag₂O to a solution of urea. Grey powder composed of slender needles. According to Müldér (B. 6, 1019), the yellow pp. got by adding NaOH to a solution of urea mixed with AgNO₃ is CON₂H₂Ag. It combines with iodine, forming CON₂H₂AgI, a greenish mass, darkened by light (Tafel & Enoch, *B.* 23, 1554).—B'₂HgO. Got by adding Hg(NO₃)₂ to a solution of urea mixed with KOH. White pp.—B'₂3HgO. White pp. formed by adding HgCl₂ to a solution of urea, and HgCl₂ changes to a yellow granular powder on boiling with water.—B'₂HgO. Formed by adding Hg(NO₃)₂ to a warm solution of urea (Dessaignes, *A.* 82, 282; Liebig, *A.* 65, 289).

Compounds with metallic salts.—B'AgNO₃. Prisms. Yields silver cyanate on

boiling with water.—B'PdCl₂. Ppd. by adding a solution of PdCl₂ to one of urea (Drechsel, *J. pr.* [2] 20, 469).—B'NaCl_{aq}. [60°–70°]. Formed by evaporation of a solution of urea and NaCl. Deliquescent prisms. Alcohol extracts urea from the compound.—B'NaNO₃. aq. Prisms (from water).—B'NH₄Cl. Deliquescent crystals.—B'₂(NH₄)₂HCl. Formed by dissolving urea in bleaching-powder solution (Beckmann, *A.* 91, 367). Large plates, sol. alcohol mixed with ether.—B'₂Mg(NO₃)₂ (Werther, *J. pr.* 35, 5).—B'₂Ca(NO₃)₂.—B'₂ZnCl₂. Very deliquescent crystals (Neubauer & Kerner, *A.* 101, 337).—B'₂CdCl₂. Needles.—B'₂Hg(NO₃)₂3HgO. Granular powder formed by mixing warm dilute solutions of urea and mercuric nitrate. At the moment of formation the pp. is flocculent.—B'₂Hg(NO₃)₂2HgO.* Formed by pouring mercuric nitrate into a solution of urea as long as a pp. is produced, and keeping the whole at 40° to 50° for some time (Liebig). Six-sided laminae.—B'₂Hg(NO₃)₂HgO. Formed by adding an acid solution of mercuric nitrate to a solution of urea nitrate. Crusts of small tabular crystals (Liebig, *A.* 85, 296).—B'₂HgCl₂. Flat crystals, v. sl. sol. cold water (W.).—B'₂Cr₂O₇3aq. Formed by the action of water on the product of the action of CrO₂Cl₂ on urea (W. J. Sell, *Pr.* 33, 267; 45, 321). Olive-green needles (from hot water). PtCl₂ added to its solution in hot water ppts. silky green needles of B'₂Cr₂Cl₂(PtCl₂)₂aq. The chromate treated with PbCl₂ forms lead chromate and a liquid from which gaseous HCl ppts. green prisms of B'₂Cr₂O₇6aq, the aqueous solution of which heated with Ag₂SO₄ gives dark-green prisms of B'₂Cr₂(SO₄)₂10aq. In a similar way green prisms of B'₂Cr₂(NO₃)₂ may be got.—B'₂Cr₂Cl₂O₇2aq. Green monoclinic crystals, got from the product of the action of CrO₂Cl₂ on urea by crystallising from conc. HClAq (1 vol.) diluted with water (9 vols.). By treatment with water it is split up into B'₂Cr₂O₇ and B'₂Cr₂Cl₂. By treatment with conc. HClAq (1 vol.) and water (6 vols.) it is converted into the salts B'₂Cr₂Cl₂O₇3aq.—B'₂Cr₂O₇4aq.—B'₂Cr₂Br₂6aq.—B'₂Cr₂Cl₂6HgCl₂.—B'₂Cr₂(C₂O₄)₂4aq.—B'₂Cr₂I₂.—B'₂Cr₂(SO₄)₂I₂.—B'₂Cr₂(CO₃)₂I₂.—B'₂Cr₂(CO₃)₂I₂.—B'₂Cr₂Br₂. Bronze-yellow tables, giving off bromine in air.—B'₂CuCl₂. Small blue crystals.

Formyl derivative NH₂.CO.NH.OH. [159°]. H.F. 13,400 (Matignon, *C. R.* 112, 1367). Formed by boiling urea with conc. formic acid (Geuther, *Z.* [2] 4, 300). Crystals, v. sol. water, being decomposed into urea and formic acid.

Acetyl derivative C₂H₃N₂O₂ &c. NH₂.CO.NHAc. **Acetureide**. Mol. w. 102. [214°]. H.F. –200 (M.). S. (alcohol) 1 in the cold; 10 at 78°. Formed by boiling urea with AcCl or Ac₂O (Zinin, *A.* 92, 405; G.; Zrde, *R. T. C.* 8, 235). Got also by the action of KMnO₄ on methyl-uracil (Behrend, *A.* 229, 29). Four-sided needles (from alcohol). Slowly but completely decomposed by pure HNO₃ with evolution of CO₂ (1 vol.) and N₂O (2 vols.) (Franchimont, *R. T. C.* 6, 215). It is not pped. by Hg(NO₃)₂.

Di-acetyl derivative CO(NHAc)₂. [153°]. A product of the action of COCl₂ on acetamide at 50° (Schmidt, *J. pr.* [2] 5, 63).

Formed also from mercuric fulminate and AcCl (Scholl, *B.* 23, 8515). Needles (from alcohol), sl. sol. cold water.

Chloro-acetyl derivative

$\text{NH}_2\text{CO.NH.CO.CH}_2\text{Cl}$. Formed from chloro-acetyl chloride and urea (Jazukovitch, *Z.* 1868, 234; Tommasi, *C. R.* 76, 640). Thin needles (from alcohol). Begins to melt at 160° .

Tri-chloro-acetyl derivative

$\text{NH}_2\text{CO.NH.CO.CCl}_3$. [150°]. Crystals (from alcohol) (De Clermont, *J.* 1874, 798; Meldola & Tommasi, *C. J.* 1874, 404; Cloez, *A. Ch.* [6] 9, 219). Nearly insol. hot water.

Bromo-acetyl derivative

$\text{NH}_2\text{CO.NH.CO.CH}_2\text{Br}$. Needles (from dilute alcohol) (Baeyer, *A.* 130, 156). Pure HNO_3 gives off CO_2 (1 vol.) and N_2O (2 vols.) (Franchimont, *R. T. C.* 6, 218).

Tri-bromo-acetyl derivative

$\text{NH}_2\text{CO.NH.CO.CBr}_3$. [148°]. Formed by the action of Br on an aqueous solution of di-bromobarbituric acid (Baeyer). Crystals, v. sol. hot alcohol. Yields crystalline $\text{B}^2\text{Ba}(\text{OH})_2\text{aq}$, v. e. sol. water.

Cyano-acetyl derivative

$\text{NH}_2\text{CO.NH.CO.CH}_2\text{Cy}$. [200°–210°] (Mulder, *B.* 12, 466). Crystalline.

Butyryl derivative $\text{NH}_2\text{CO.NH.C}_4\text{H}_7\text{O}$

[176°]. Formed from urea and butyryl chloride (Moldenhauer, *A* 94, 101). Plates.

Isovaleryl derivative $\text{C}_4\text{H}_7\text{O}_2$

[191°]. Minute prisms, v. sl. sol. water.

Carbonyl derivative $\text{CO}(\text{NH.CO.NH})_2$

Formed by heating urea with COCl_2 at 100° (E. Schmidt, *J. pr.* [2] 5, 39; Emich, *M.* 10, 347). Powder composed of minute crystals, v. sl. sol. cold water and alcohol. Decomposed by heat into NH_3 and cyanuric acid. Boiling KOH also produces cyanuric acid.— B^2HgO : crystalline powder, insol. water.

Succinyl derivative

$\text{C}_4\text{H}_5\text{O}_2(\text{NH.CO.NH})_2$. Formed by heating urea (2 mols.) with succinyl chloride (1 mol.) at 65° (Conrad, *J. pr.* [2] 9, 301). Colourless powder, v. sl. sol. hot water.

Methyl-malonyl derivative

$\text{CHMe.C}_2\text{O}_2\text{N}_2\text{H}_2\text{CO}$. [192°]. Formed by heating methyl-malonic acid with urea and PCl_5 (Franchimont & Klobbie, *R. T. C.* 7, 22). Pointed plates, v. sol. water and alcohol.

Benzoyl derivative $\text{NH}_2\text{CO.NH.Bz}$

[c. 200°]. S. (alcohol) 1 in the cold; 4 at 78° . Formed by heating urea with BzCl or Bz_2O at 150° (Zinin, *A.* 92, 404; Geuther, *Z.* [2] 4, 299). Four-sided plates (from alcohol), insol. ether).

Di-benzoyl derivative $\text{CO}(\text{NEBz})_2$

[210°] (S.); [197°] (H.). A product of the action of COCl_2 on benzamide at 165° (E. Schmidt, *J. pr.* [2] 5, 58). Formed also by heating guanidine carbonate with Bz_2O at 100° (Creath, *B.* 7, 1739) and by treating mercuric fulminate with BzCl (Holleman, *R. T. C.* 10, 72; *B.* 23, 2998, 3742). Needles (from alcohol), sl. sol. water. Aniline at 180° gives NEBz , benzamide, benzanilide, and *s*-di-phenyl-urea.

Di-benzoyl derivative $\text{NH}_2\text{CO.NBz}$

[c. 197°]. Formed by heating sodium benzoyle cyanamide NaBzN.CN with BzCl , followed by boiling alcohol (Buddéus, *J. pr.* [2] 42, 97). White needles.

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m-Nitro-benzoyl derivative

$\text{NH}_2\text{CO.NH.CO.C}_6\text{H}_4\text{NO}$; [1:8]. Plates (Griess, *B.* 8, 222).

m-Amido-benzoyl derivative $\text{C}_6\text{H}_4\text{N}_2\text{O}_2$

Formed by boiling the preceding body with aqueous ammonium sulphide (G.). Needles (from water), decomposing at 200° .— $\text{B}^2\text{HCl aq}$: needles.— $\text{B}^2\text{H.PtCl}_4$.

(β)-Naphthoyl derivative

$\text{NH}_2\text{CO.NH.CO.C}_{10}\text{H}_7$. [215°]. Formed from naphthoyl chloride and urea (Vieth, *A.* 180, 319). Minute needles, m. sol. alcohol, v. sl. sol. benzene.

Di-(β)-naphthoyl urea [286°] (Ekstrand, *B.* 20, 1853). Needles.

Lactyl derivative v. LACTYL-UREA.

Glycolyl derivative v. HYDANTOIN.

Reference.—OXY-UREA.

UREA CARBOXYLIC ACID v. ALLOPHANIC ACID.

UREA CHLORIDES. A name sometimes used to denote alkyl-carbamic chlorides X.NH.CO.Cl .

URECHITIN $\text{C}_{22}\text{H}_{32}\text{O}_8$

Occurs, together with urechitoxin, in the leaves of *Urechites suberecta*, growing in Jamaica (Bowrey, *C. J.* 33, 252). Crystallises from alcohol in needles (containing aq), tastes bitter. It is very poisonous (*Pr.* 27, 309). Nearly insol. water, m. sol. ether. Appears to be a glucoside. Conc. H_2SO_4 forms a yellow liquid, turning red, and finally purple, especially in presence of an oxidising agent.

Urechitoxin $\text{C}_{12}\text{H}_{16}\text{O}_8$. Bitter poison, split up by acids into sugar and urechitoxetin.

UREIDES. Compounds obtained by elimination of water between urea and an acid or an aldehyde. * Many of them may be represented as amides in which NH_2 is replaced by NH.CO.NH_2 .

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URETHANE v. CARBAMIC ETHER.

ISURETINE v. FORMAMIDOXIM.

URIC ACID $\text{C}_5\text{H}_4\text{N}_2\text{O}_6$ &c.

$\text{CO} \begin{matrix} \text{NH.CO.C.NH} \\ \text{NH} \end{matrix} \text{CO}$ (Medicus, *A.* 175, 243; Fischer, *B.* 17, 329, 1776). Mol. w. 168. S.G. 1.87. H.C.p. 461,400 (Berthelot, *C. R.* 110, 887; Matignon, *C. R.* 110, 1267); 462,500 (Stohmann, *J. pr.* [2] 44, 590). H.C.v. 462,700 (M.). H.F. 148,100 (M.). S. -002 at 0° ; -006 at 20° ; -0625 at 100° (Blarez & Denigès, *C. R.* 104, 1847; cf. Gwyrod, *Pr.* 35, 63).

Occurrence.—In urine and in urinary calculi (Schöde, *A.D.* 1776; Liebig & Wöhler, *A.* 26, 241; Horbaczewski, *M.* 12, 221). * About .5 g. is daily excreted in human urine. Uric acid occurs in urine of carnivora, herbivora (Mittelbach, *H.* 12, 463), and of birds. Serpent's urine is chiefly composed of acid ammonium urate. A considerable quantity occurs in the blood of gouty subjects, and sodium urate is deposited as 'chalk stones.' Very small quantities are normally present in the liver, lungs, brain, and blood. It occurs in the green gland of the fresh-water crayfish (Griffiths, *Pr.* 36, 187). Urea, glycocholl, leucine, and aspartic acid give, to bowls appear in the urine as uric acid (Jaffé & Meyer, *B.* 10, 1930; Knierim, *B.* 10, 1930).

Synthesis.—1. By rapidly heating glycocholl (1 pt.) with urea (10 pts.) to 230° (Horbaczewski, *B.* 15, 2678; *M.* 3, 796; 6, 856).—2. By heating

8 H

urea with tri-chloro-lactic acid or its amide (Horbaczewski, *M.* 8, 201, 584).—8. By preparing methyl-uracil from acetoacetic ether and urea; converting methyl-uracil into nitro-uracil carboxylic acid by treatment with fuming HNO_3 ; boiling the carboxylic acid with water, and reducing the resulting nitro-uracil to amido-uracil, and finally to isobarbituric acid by means of tin and HClAq ; oxidising the isobarbituric acid to isodialuric acid; and heating the isodialuric acid (1 pt.) with urea (1 pt.) and H_2SO_4 (6 pts.) (Behrend & Roosen, *A.* 251, 235).—4. By fusing urea (4 g.) with cyano-acetic acid (1 g.) (Forináněk, *B.* 24, 3419).

Preparation.—1. Serpent's urine is dissolved in boiling KOH aq, filtered, and the uric acid ppd. by HCl or dilute H_2SO_4 . If the uric acid is much coloured a little KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ (Gibbs, *Am. S.* [2] 48, 215) should be added to the boiling alkaline solution before ppn.—2. Guano is boiled with borax (1 pt.) and water (120 pts.), and the solution of sodium urate thus obtained ppd. by HCl .—3. Guano is extracted with dilute HCl aq, and the residue dissolved in conc. H_2SO_4 , and ppd. by water.

Properties.—White anhydrous scales (by ppn.). When slowly deposited from dilute solutions (e.g. urine) it separates as large crystals (containing 2aq). Nearly insol. water, insol. alcohol and ether. Sol. conc. H_2SO_4 , and reppd. by water. Its solution in hot H_2SO_4 deposits on cooling a deliquescent compound of uric acid with H_2SO_4 . Uric acid is m. sol. glycerin, hot NaOAc , and sodium phosphate. Lithium carbonate (1 pt.) dissolved in water (90 pts.) can dissolve uric acid (4 pts.). Aqueous K_2CO_3 also dissolves uric acid.

Reactions.—1. Decomposed by heat, without fusion, yielding HCy and a sublimate of cyanuric acid, ammonium cyanate, urea, and ammonium carbonate, and leaving a carbonaceous residue. 2. Water at 180° forms mycomelic acid (Hlasivetz, *A.* 103, 211).—3. Potash-fusion yields NH_3 and potassium oxalate, carbonate, and cyanate.—4. Chlorine and bromine in presence of water yield alloxan, urea, and parabanic acid (Hardy, *A. Ch.* [4] 2, 372). Alloxan is also produced by iodine by HNO_3 , and by MnO_2 and H_2SO_4 .—5. Boiling with water and PbO yields allantoin. Allantoin is also produced by ozone (Gorup-Besanez, *A.* 110, 94), alkaline K_2FeCy_6 , KMnO_4 (Claus, *B.* 7, 226), and MnO_2 and water. 6. Pure HNO_3 decomposes uric acid in the cold, with evolution of CO_2 (14 vols.), N_2O (24 vols.), and nitrogen (4 vols.) (Franchimont, *R. T. C.* 6, 222). 7. KNO_3 and HOAc yield urilinic acid (Sokoloff, *Z.* [2] 5, 78) and stryphnic acid (Gibbs, *Am. J.* [2] 48, 215).—8. HIAq at 165° forms glycoecoll. NH_3 , I , and CO_2 (Strecker, *Z.* [2] 4, 215).—9. Exposed to the air in alkaline solution it yields oxonic and uruxanic acids.—10. A dilute solution of sodic urate absorbs oxygen from the air at 35° according to the equation $\text{C}_4\text{H}_4\text{N}_4\text{O}_6 + \text{O} + 2\text{H}_2\text{O} = \text{C}_4\text{H}_4\text{N}_4\text{O}_8$ (uroxanic acid). Uric acid in dilute NaOH solution is completely decomposed by 35 days' digestion at 85° (Nencki & Sieber, *J. pr.* [2] 56, 18). 5 g. uric acid dissolved in 200 c.c. water and 20 g. potash disappeared in 5 days. However, if no oxygen be present the uric acid is not affected.—11. In fermenting urine uric

acid is completely split up into CO_2 and NH_3 (Sestini, *G.* 20, 138).

Detection.—Uric acid may be recognised by its insolubility in water and HClAq , by its crystalline character under the microscope, and especially by the murexide reaction. When evaporated with HNO_3 on a water-bath it leaves an orange residue, which is coloured violet-red by ammonia and violet-blue by potash. A solution of uric acid in aqueous Na_2CO_3 produces a dark-brown spot of reduced silver when added to paper moistened with AgNO_3 (Schiff, *A.* 109, 65). Uric acid (1 mol.) reduces boiling Fehling's solution, forming a pp. of Cu_2O (1 mol.) (W. Müller, *J. Th.* 1881, 73). In presence of KOH uric acid dissolves CuO , forming a blue solution, which slowly deposits white cuprous urate. The compound $\text{C}_4\text{H}_4\text{N}_4\text{O}_6\text{Cu}_2\text{O}$ is ppd. when an alkaline solution of uric acid is treated with Fehling's solution and hydroxylamine hydrochloride (Balke, *J. pr.* [2] 47, 546). Uric acid evaporated with a little dilute HNO_3 gives a blue colour on shaking with H_2SO_4 and benzene containing thiophene (Denigès, *J. Ph.* [5] 18, 161).

Estimation in urine.—1. Urine (500 c.c.) is concentrated, HCl is added, and after twenty-four hours the pp. is collected and weighed. Uric acid may be separated from xanthine by ppn. with conc. H_2SO_4 (Horbaczewski, *H.* 18, 341; cf. Wulff, *H.* 17, 334).—2. Urine (200 c.c.) is mixed with conc. Na_2CO_3 aq (10 c.c.), and after an hour conc. NH_4Cl aq (20 c.c.) added. After forty-eight hours the pp. is collected, washed with HCl (1 pt. of S.G. 1.125), diluted with water (10 pts.), the washings allowed six hours to deposit any dissolved uric acid, the combined pps. washed with alcohol and dried at 110° (Salkowski, *Pr.* 16, 373). Uric acid may also be ppd. as ammonium urate by saturating urine with solid NH_4Cl (30 g. to 100 c.c.) (Hopkins, *Pr.* 52, 93).—3. Fresh urine is mixed with very dilute (15 p.c.) NaOHAq , filtered from phosphates, and diluted to S.G. 1.010. To 300 c.c. of this solution is added 50 c.c. of magnesia mixture (MgSO_4 , 7aq (1 pt.), NH_4Cl (2 pts.), NH_4Aq (4 pts. of S.G. 924), and water (8 pts.)). The pp. is filtered off, and 175 c.c. of the filtrate mixed with 5 g. CaCO_3 and 5 c.c. of a 8 p.c. solution of AgNO_3 . The pp. is washed and dried, and a nitrogen estimation made by Kjeldahl's method (Camerer, *Z. B.* 26, 84; cf. Salkowski, *Pr.* 5, 819).—4. Urine (25 c.c.) is mixed with NaHCO_3 (1 g.), and NH_4Aq (2 to 3 c.c.), and ammoniacal AgNO_3 (1 to 2 c.c. of a solution of 5 g. AgNO_3 in 100 c.c. water, to which NH_4Aq is added till the ppd. Ag_2O is just re-dissolved). The pp. is collected, washed, dissolved in HNO_3 , and the silver determined volumetrically by the sulphocyanide method (Haycraft, *Pr.* 25, 167; 30, 648). This method is liable, according to Salkowski (*H.* 14, 31) and Gossage (*Pr.* 44, 384), to an error which may amount to 60 p.c. The error is partly due to variations in composition of the silver urate, and partly to presence of bodies of the xanthine group (Derode, *Bl.* [3] 7, 863). V. also Herrmann, *H.* 12, 496; Ozapek, *H.* 12, 502).—5. In a solution containing not more than 0.25 p.c. of uric acid 1 c.c. of decinormal permanganate is reduced by 0.074 g. uric acid (Blarez & Denigès, *C. R.* 104, 789).—6. By treat

ment with a standard iodine solution in presence of alkali (Kresidl, *M.* 14, 109).

Salts.— $(\text{NH}_4)\text{HA}$. S. °06 at 15°. Slender needles.— $(\text{NH}_4)_2\text{HA}$.— $(\text{NH}_4)_3\text{H}_2\text{A}$. (Maly, *J.* 1863, 621).— K_2A . S. 8 at 16°. Small needles.— KHA . S. 18 at 20°. Amorphous.— Na_2A aq. S. 1.5. Nodules.— NaHA aq (dried at 100°). Crystalline powder. S. °09 at 15°; °8 at 100°. Occurs as an amorphous urinary deposit.— LiHA . S. 27 at 20°; °9 at 40°; 2.5 at 100° (Schilling, *A.* 122, 241).— BaA aq (dried at 100°). Granular pp. S. °13 in the cold.— BaH_2A , 2aq (dried at 100°). Amorphous, insoluble powder (Behrend a. Roosen, *A.* 251, 250).— CaA . S. °066 in the cold; °07 at 100°.— CaH_2A , 2aq. S. °15 in the cold; °37 at 100°. More sol. KClAq .— SrA 2aq. Minute stellate groups of needles. S. °023 in the cold; °055 at 100°.— SrH_2A , 2aq.— MgH_2A , 6aq. S. °08 in the cold; °6 at 100°.— PbH_2A , (dried at 100°). Insol. water.— PbA (dried at 100°).— Cu_2A aq.— $\text{Cu}_2\text{A}_2(\text{OH})_2$, 4aq; green pp.

Reference.—METHYL-URIC ACID.

Iso-uric acid $\text{C}_5\text{H}_7\text{N}_3\text{O}_6$. Formed by boiling cyanamide (1 pt.) with an aqueous solution of alloxantin (2 pts.) (Mulder, *B.* 6, 1236; 7, 1633). Powder, almost insol. water. Oxidised by boiling with I and water. Its solution in K_2CO_3 reduces AgNO_3 .

Pseudo-uric acid $\text{C}_5\text{H}_7\text{N}_3\text{O}_6$, i.e.

$\text{CO} < \text{NH.CO} > \text{CH.NH.CO.NH}_2$. Formed by the action of KCyO on uramil (Baeyer, *A.* 127, 3), and by heating uramil with urea at 180° (Grimaux, *Bl.* [2] 31, 535). White crystalline powder composed of small prisms, v. sl. sol. water. HNO_3 yields alloxan. Boiled with water and PbO_2 it yields oxalic acid, but no allantoin. H_2SO_4 at 150° forms xanthinone.— $(\text{NH}_4)\text{HA}$ aq.— KHA aq; scales.— NaHA 2aq; groups of prisms, v. sol. hot water.— BaA 5aq; groups of slender needles.

URINILIC ACID $\text{C}_5\text{H}_7\text{N}_3\text{O}_6$. Formed by the action of KNO_3 and HOAc on uric acid (Sokoloff, *Z.* 1869, 78). Prisms (from water).— K_2HA . Prisms, v. e. sol. water. CaA . Crystalline pp. insol. water and HOAc .— SrA .— BaA .— CdHA 8aq.— CuHA 4aq. Slender red needles.— AgHA . Pp.— Ag_2A . Gelatinous pp. quickly blackening in light.

UROBILIN.

Occurrence.—Often in urine (Jaffé; Disqué, *H.* 2, 271; *C.* C. 1878, 711; Eikholz, *J. Physiol.* 14, 326). In bile, especially of the moose.

Preparation.—Urine containing urobilin is ppd. by lead acetate and sub-acetate until the absorption band at F is removed. The pp. is extracted with alcohol, acidified with HCl or H_2SO_4 , filtered, diluted with water, and extracted with chloroform.

Properties.—A red amorphous, shiny substance. Prepared as above it contains HCl or H_2SO_4 , as the case may be. Its spectrum exhibits a dark band at F, destroyed by NH_3 , but on adding NaOH another band near the red is formed (MacMunn, *Pr.* 80, 250; 81, 26, 206; v. also *HYDROBILIN*, this vol. p. 273).

Detection and estimation in urine: Jolles, *H.* 18, 545; Studensky, *C.* C. 1893, ii. 668.

UROCANINIC ACID $\text{C}_5\text{H}_7\text{N}_3\text{O}_6$. [213°]. Occurs in dog's urine (Jaffé, *B.* 7, 1669; 8, 811).

Prisms (containing 4aq), v. sol. hot water, insol. alcohol and ether. Decomposed by fusion into CO_2 and urocannine $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_6$, an amorphous base yielding $\text{B}^+\text{H}^-\text{PtCl}_6^-$ — $\text{HA}^+\text{H}^-\text{Cl}$: needles, v. e. sol. water.— $\text{HA}^+\text{H}^-\text{NO}_3$: crystalline pp. insol. dilute HNO_3 , v. sol. water.— $\text{HA}^+\text{H}^-\text{SO}_4$. Minute needles and plates.

UROCHLORALIC ACID $\text{C}_5\text{H}_7\text{N}_3\text{O}_6$ (?) [142°]. S. (ether) 4. Found in the urine after administration of chloral (Von Mering a. Musculus, *B.* 8, 662; *H.* 6, 483; Kütz, *C.* C. 1881, 486). Silky needles, v. e. sol. water and alcohol. Decomposed by boiling dilute H_2SO_4 into tri-chloroethyl alcohol and glycuronic acid $\text{C}_6\text{H}_9\text{O}_6$.— NaA .— KA .— BaA : satiny plates (from ether-alcohol).

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UROLEUCIC ACID $\text{C}_5\text{H}_7\text{N}_3\text{O}_6$. [133-5°]. An acid occurring in human urine which darkens on addition of alkalis (Kirk, *Brit. Med. Journ.* [1888] 2, 232). Crystals. Its solution is ppd. by $\text{Pb}(\text{OAc})_2$ and gives a transient green colour with very dilute FeCl_3 . FeCl_3 colours the crystals red.

UROMELANIN $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_6$. A black substance which separates on treating urine with H_2SO_4 or HClAq in presence in air (Thudichum, *J. pr.* 104, 257; *C.* R. 106, 1803; Ploetz, *H.* 8, 89; Udranski, *H.* 11, 537; 12, 32; this vol. p. 274). It yields $\text{C}_{10}\text{H}_{10}\text{AgN}_2\text{O}_6$ (Thudichum).

URONITROTOLUOLIC ACID $\text{C}_{10}\text{H}_{11}\text{N}_3\text{O}_6$. Occurs in urine of dogs after a dose of o-nitrotoluene (Jaffé, *H.* 2, 47). Very deliquescent. Asbestos-like mass, v. e. sol. water and alcohol. Decomposed by dilute H_2SO_4 into o-nitro-benzyl alcohol and a syrupy acid. Salts.— BaA : crystalline powder, v. e. sol. water, insol. alcohol.— $\text{CO}(\text{NH}_2)_2\text{HA}$ 2aq. [149°]. Needles, v. e. sol. water, sl. sol. cold alcohol.

UROROSEIN v. this vol. p. 274.

UROSULPHINIC ACID $\text{C}_5\text{H}_7\text{N}_3\text{SO}_6$. Formed by heating thio-uramido-barbituric acid (1 pt.) with H_2SO_4 (2 pts.) at 160° (Nencki, *B.* 4, 724; 5, 45). Nodules (from hot HClAq). Its K salt crystallises in needles, m. sol. cold water.

UROXANIC ACID $\text{C}_5\text{H}_7\text{N}_3\text{O}_6$. Formed by leaving a solution of uric acid (5 g.) in water (200 c.c.) containing KOH (20 g.) to stand for 5 days at 35°, neutralising by HOAc , filtering, and evaporating (Nencki a. Sieber, *J. pr.* [2] 24, 604; cf. Städeler, *A.* 78, 286; 80, 119; Strecker, *A.* 155, 177; Mulder, *B.* 8, 1291). Tetrahedra, sl. sol. cold water, insol. alcohol. Decomposed by boiling water into CO_2 , urea, and allanturic acid.— K_2A 43aq. Four-sided pearly plates, v. spl. hot water.— CaA 4aq.— BaA 5aq.— PbA 4aq. Insol. water.— Ag_2A : flocculent pp., turned red by light.

URSONE $\text{C}_{10}\text{H}_{10}\text{N}_2\text{O}_6$ 2aq. [265°] (Gintl, *M.* 14, 255). Occurs in the leaves of the bear-berry (*Arctostaphylos Uva-ursi*) (Trommsdorff, *Ar. Ph.* [2] 80, 278; Hlasiwetz, *J. pr.* 68, 123). Needles, insol. water, acids, and alkalis, sl. sol. alcohol and ether. Conc. H_2SO_4 added to its solution in Ac_2O gives a red colour, changing through blue to green. Does not react with hydroxylamine or phenyl-hydrazine. Reduced by HI and F at 860° to $\text{C}_{10}\text{H}_{11}$ (256°-267°).

Acetyl derivative [264°].

Benzoyl derivative [214°].

URUSHIC ACID $C_{11}H_{16}O_8$. S.G. 2.5-2.85. Occurs in urushi or Japanese lacquer (Yoshida, *C. J.* 43, 479). Dark, pasty mass, v. sol. benzene and ether, insol. water. Br in CS, forms $C_{11}H_{12}Br_2O_8$. HNO_3 forms $C_{11}H_6(NO_3)_2O_8$, which forms Fe_2A_3 . Chromic acid mixture forms oxo-urushic acid $C_{11}H_6O_8 \cdot PbA_4$, (dried at 100°). $[110^\circ-115^\circ]$. Flocculent pp. $-FeH_2A_{12}$ 2aq. $-FeH_2A_4$. Deep-black pp.

USNETIC ACID $C_8H_6O_8$. [172°]. Occurs in small quantity, together with usnic acid, in the lichen *Usnea barbata* (Hesse, B. 10, 1326). Flat prisms (from alcohol), v. sol. ether. $FeCl_3$ colours its alcoholic solution: bluish-violet. Bleaching-powder does not colour its alkaline solution. Is perhaps identical with decarbusnic.

USNIC ACID $C_{18}H_{16}O_8$ (Salkowski; Paterno) or $C_{18}H_{16}O_9$ (Hesse), or $C_{18}H_{16}O_{10}$ (Stenhouse) a. Groves, *C. J.* 39, 234). *Carbusic acid*. [156°⁴² cor.]. S. (ether) -3 at 20°. Occurs in the lichens *Usnea barbata*, *Usnea florida*, *Leora sordida* (Knop, A. 49, 103; Rochedler a. Heldt, A. 48, 12; Thomson, A. 53, 225; Stenhouse, *Pr.* 18, 222; A. 68, 97, 114; 155, 51; Hesse, A. 117, 343; Paterno, G. 8, 225; Salkowski, B. 8, 1459). Sulphur-yellow monoclinic crystals, sl. sol. alcohol, v. sol. hot ether and benzene. Does not yield betorcin when heated. Conc. H_2SO_4 forms usnicolic acid $C_{22}H_{20}O_{10}$ [213°] crystallising in small ~~years~~-ish prisms (Stenhouse a. Groves, *C. J.* 39, 236). When it is heated with an alcoholic solution of aniline it yields the anilide $C_{24}H_{18}O_{10}$ (NHPh), crystallising from alcohol in pale-yellow plates [171°], and forming in KOH aq a yellow solution from which HCl ppts. $C_{22}H_{22}NO_8$ [171°].

Salts.— $\text{NaC}_{10}\text{H}_{11}\text{O}_8$ 2aq (Spica, *G.* 12, 432). Pale-yellow, silky needles. — $\text{KC}_{10}\text{H}_{11}\text{O}_8$ 3aq or $\text{KC}_{10}\text{H}_{11}\text{O}_8$ 3aq. Pale-yellow plates (from 50 p.c. alcohol) (Hesse, *B.* 10, 1325). — $\text{KC}_{10}\text{H}_{11}\text{O}_8$ aq or $\text{KC}_{10}\text{H}_{11}\text{O}_8$ aq. Yellow prisms (from 93 p.c. alcohol). — CuA' : green pp.

4. Decarbusnein $C_{11}H_{16}O_8$. [175°]. Formed by heating usnic acid (1 pt.) with alcohol ($3\frac{1}{2}$ pts.) at 150° (Paterno, G. 12, 234). Yellow, silky needles, sol. hot alcohol, sl. sol. water and ether. Not coloured by $FeCl_3$. Not attacked by $AcCl$. Reduces warm ammoniacal $AgNO_3$. Boiling KOHq in absence of air splits it up into HOAc and decarbusnic acid $C_{11}H_{16}O_8$, which crystallises from alcohol in lemon-yellow "prisms" [199°] and yields, when boiled with Ac_2O , two acetyl derivatives $C_{11}H_{14}AcO_8$ [148°] (isomeric with decarbusnein) and $C_{11}H_{14}AcO_8$ [181°].

Pyrounic acid $C_{12}H_{10}O_5$ (P.); $C_6H_5O_4$ (Sal-kowski, *B.* 8, 1461). [197²]. Formed, together with pyrounsenic acid, by boiling usnic acid (2 pts.) with KOH (5 pts.) and water (5 pts.) in an atmosphere of hydrogen (Paterno, *G.* 3, 13; 12²

242). Shining scales (from ether), v. sol. alcohol, sl. sol. ether. Its alkaline solution absorbs oxygen from the air, turning green and ultimately brown. Reduces ammoniacal AgNO_3 readily. Ac_2O yields an acetyl derivative $[\text{265}^\circ]$. Alcohol and HCl form an ether $[\text{147}^\circ]$. Pyro-unsic acid is split up on dry distillation in a current of H into CO_2 and unsuele $\text{C}_8\text{H}_{10}\text{O}_2$, which crystallises from alcohol in yellow prismatic tablets $[\text{176}^\circ]$ and is converted by AcCl into a di-acetyl derivative $[\text{142}^\circ]$.

Pyrosuccinic acid $C_4H_4O_6$, *z.* $C_4H_4O_6$. [1867]. Formed by boiling succinic acid (10 pts.) with KOH (25 pts.) and water (25 pts.) for 15 minutes (Paterno, G. 12, 238). Colourless plates or needles (from alcohol). Ac_2O yields $C_4H_2Ac_2O_6$ [1687]. When heated in a current of H_2 , pyrosuccinic acid is split up into CO_2 and unsateloic acid $C_4H_4O_4$, which crystallises from dilute alcohol in yellowish needles [1797].

(β)-Usnic acid v. CLADONIC ACID.

UVIC ACID *v.* PYROTRITARIC ACID.

UVINONE $C_{14}H_{10}O_4$ i.e.

$\text{O} \begin{array}{c} \text{CMe}:\text{C}:\text{CO}:\text{C}:\text{CMe} \\ \text{CMe}:\text{C}:\text{CO}:\text{C}:\text{CMe} \end{array} \text{O} \text{ (?) [247°]. Formed, to the extent of 2 p.c., by distilling pyrotritaric acid (Dietrich a. Paal, *B.* 20, 1086). Yellow needles (by sublimation), sol. HOAc, v. sl. sol. alcohol. Conc. H_2SO_4 forms a solution with green fluorescence. Br at 100° forms crystalline $\text{C}_8\text{H}_4\text{Br}_2\text{O}_4$.$

UVITIC ACID $C_9H_8O_4$ *i.e.*

$\text{C}_6\text{H}_5\text{Me}(\text{CO}_2\text{H})_2$ [1:3:5]. *Mesidic acid*. Mol. w. 180. [288*]. H.C.v. and p. 928, 900. H.F. 193, 100 (Stohmann, *J. pr.* [2] 40, 128). Formed together with uvitonic acid, by boiling pyruvic acid with baryta-water (Finck, A. 192, 184). Formed also by oxidation of mesitylene or mesitylenic acid (Fittig, A. von Furtenbach, Z. [2] 4, 1; A. 147, 255), by oxidation of di-methyl-ethyl-benzene (Wroblewsky, A. 192, 217), and by heating $\text{C}_6\text{H}_5\text{Me}(\text{SO}_2\text{NH}_2)(\text{CO}_2\text{H})$ with conc. HClAq at 230° (Hall, A. Remsen, *Am. J.* 2, 136). Slender needles (from water), v. sl. sol. hot water, m. sol. alcohol and ether. Yields toluene on heating with soda-lime (Baeyer, Z. [2] 4, 119). The Ca salt heated with lime yields m-toluic acid (Böttlinger, A. Ramsay, A. 168, 255). Chromic acid mixture oxidises it to trimesic acid.

Salts.— K_2A'' : plates (from alcohol), v. sol. water.— BaA'' aq.— CaA'' aq.— Ag_2A'' . Nearly insol. cold water.

Ethyl ether Et:A". [35°]. 'Crystalline.

References.—AMIDO-, BROMO-, NITRO-, and OXY-UNITIC ACID.

Isouvicic acid v. CARBOXY-PHENYL-ACETIC ACID.

Uvitonic acid v. METHYL-PYRIDINE-DICARB-
OXYLIC ACID.

VALERAL o. VALERIC ALDEHYDE.

VALERAL-DI-ACETONAMINE v. *Pentyl-*
idene di-ACETONAMINE.

VALERALDINE $C_5H_{11}NS$. *Thiovaleraldine*.

[41°]. Formed by the action of H_2S on isovaleric aldehyde ammonia suspended in water (Beissonhütz, A. 90, 109; Parkinson, A. 90, 119). Formed also from thioisovaleric aldehyde and dry NH_3 (Schröder, B. 4, 468). Plates (from

ether), with powerful smell, sol. alcohol, insol. water.—B.HCl. Needles, sol. water.

VALECREATININ v. METHYL-GUANIDO-VALERIC ACID.

VALERIAN OIL. An essential oil obtained from the root of *Valeriana officinalis*. It contains a terpene $C_{10}H_{16}$ (156°) [α]_D = -21°, a camphene, borneol $C_{15}H_{26}O$, di-bornyl oxide ($C_{10}H_{16}O$) (285°-290°), formyl-, acetyl-, and valeryl-borneol, and a little valeric acid (Gerhardt, *A. Ch.* [3] 7, 275; Pierlot, *A. Ch.* [3] 56, 291; Bruylants, *J. Ph.* [4] 27, 349; B. 11, 452; Haller, *C. R.* 103, 161; Oliviero, *G. R.* 117, 1096).

n-VALERIC ACID $C_5H_{10}O_2$ i.e. $CH_3(CH_2)_3CO_2H$. Mol. w. 102. (180° cor.). S.G. $\frac{2}{3}$ 9562 (Zander, *A.* 224, 65); $\frac{1}{4}$ 9446; $\frac{3}{8}$ 9375 (Perkin); $\frac{2}{3}$ 9298 (Brühl). C.E. (0°-10°) 00098 (Z.). S. 3-5 at 16°. S.V. 130-0 (Z.). M.M. 5-513 at 13-6°. μ_D = 1.4093. R_D = 43-16 (Brühl). H.F. 137,800 (Stohmann, *J. pr.* [2] 49, 99). Occurs in crude wood vinegar (Grodzki a. Krämer *B.* 11, 1358).

Formation.—1. By saponifying its nitrile (n-butyl cyanide) (Lieben a. Rossi, *A.* 159, 58; *G.* 1, 239).—2. By oxidation of n-amyl alcohol (L. a. R.).—3. By the action of metallic silver on a mixture of EtI and β -iodopropionic acid (W. von Schneider, *Z.* [2] 5, 348).—4. By oxidising α -oxy-n-caproic acid (Erlenmeyer, *B.* 9, 1840).—5. By heating β -acetyl-propionic acid with HI and P at 200° (Kehrer a. Tollens, *A.* 206, 233).—6. By reducing β -acetyl-propionic acid with sodium-amalgam (Wolff, *A.* 208, 110).—7. By heating n-propyl-malonic acid at 180° (Juslin, *B.* 17, 2504; Furth, *M.* 9, 308).—8. By fermentation of calcium lactate (Fitz, *B.* 13, 1309; 14, 1044). 9. By heating the lactone of γ -oxy-n-valeric acid with HIAq and P at 240° (Fittig, *A.* 226, 346).—10. A product of oxidation of castor oil by dilute HNO_3 (Wahlfors, *B.* 22 *Ref.*, 438).

Properties.—Liquid, smelling like butyric acid.

Salts.—KA'. Plates (from alcohol).—CaA'. aq. S. 10-267 at 0°; 8-144 at 60°. Least soluble at 60°-70° (F.).—CaA'. 1½ aq (Schürlemmer, *A.* 161, 270).—BaA'. S. 21-693 at 0°; 23-076 at 80°.—MnA'. aq.—CuA'. minute green needles. More sol. cold than hot water.—ZnA'. S. 2-6 at 25°.—AgA'. S. 229 at 3°; 641 at 70-5°.

Methyl ether MeA'. (127-3°). S.G. $\frac{2}{3}$ 9097 (G.); $\frac{2}{3}$ 8795. C.E. (0°-10°) 00106. S.V. 149-1 (Gartenmeister, *A.* 233, 273). μ_D = 1.3997. R_D = 50-7.

Ethyl ether EtA'. Mol. w. 130. (144-7° cor.). S.G. $\frac{2}{3}$ 8039 (G.); $\frac{2}{3}$ 8705 (Lieben a. Rossi, *A.* 165, 117); $\frac{2}{3}$ 8661 (Brühl). S.V. 174-3. C.E. (0°-10°) 00111. μ_D = 1.402. R_D 58-03 (B.).

n-Propyl ether PrA'. (167-5°). S.G. $\frac{2}{3}$ 8888. C.E. (0°-10°) 00106 (G.). S.V. 197-8.

n-Butyl ether C₄H₉A'. (185-8°). S.G. $\frac{2}{3}$ 8847. C.E. (0°-10°) 00101. S.V. 222-1.

n-Amyl ether C₅H₁₁A'. Mol. w. 172. (203-7°). S.G. $\frac{2}{3}$ 8812 (G.); $\frac{2}{3}$ 8568 (Brühl). C.E. (0°-10°) 00097. S.V. 245-8. μ_D 1.417. R_D 80-48.

n-Hexyl ether C₆H₁₃A'. (223-8°). S.G. $\frac{2}{3}$ 8797. C.E. (0°-10°) 00096. S.V. 272-0.

n-Heptyl ether C₇H₁₅A'. (243-6°). S.G. $\frac{2}{3}$ 8786. C.E. (0°-10°) 00090. S.V. 297-4.

n-Octyl ether C₈H₁₇A'. (260-2°). S.G. $\frac{2}{3}$ 8784. C.E. (0°-10°) 00088. S.V. 322-6.

Amide C₅H₉CO.NH₂. Mol. w. 101. (116°). Pearly plates (Weidel a. Ciamician, *B.* 13, 69). V. sol. water, alcohol, and ether.

Nitrile C₅H₉CN. **n-Butyl cyanide.** (140°). S.G. $\frac{2}{3}$ 816 (Lieben a. Rossi, *A.* 158, 171). Formed, together with amylamine, by allowing a mixture of hexoic amide (1 mol.) and bromine (2 mols.) to run into a 10 p.c. solution of NaOH (Hofmann, *B.* 17, 1410).

Isovaleric acid (CH₃)₂CH.CH₂CO₂H. **Isopropyl-acetic acid.** (176° cor.). S.G. $\frac{1}{2}$ 9336; $\frac{3}{8}$ 9261 (Perkin); $\frac{3}{8}$ 931 (E. a. H.). M.M. 5-655 at 16°. S. 4-24 at 20°.

Vapour tension: Richardson, *C. J.* 49, 767.

Heat of neutralisation: Gal a. Werner, *Bl.* [2] 46, 801.

Occurs in the fat of *Daphninum Phocæna* (Chevreul [1817], *Corps gras*, pp. 99, 209), in valerian root (Grote *B.* J. 11, 225; Trommsdorff a. Ettling, *A.* 4, 229; G. 176), in the root of *Angelica Archangelica* (Meyer a. Zenner, *A.* 55, 828), in the root of *Athamanta Oroselinum*, in the bark of the alder tree, in the berries and bark of the Guelder rose (*Viburnum Opulus*) (Morro, *A.* 55, 330), in the root of *Viburnum prunifolium* (Allen, *Ph.* [3] 11, 418), and in oil of geranium (O. Jacobsen, *A.* 157, 232). A valeric acid occurs in rosin oil (Lwoff, *B.* 20, 1017) and in yolk of wool (suint) (Buisine, *Bl.* [2] 48, 639).

Formation.—1. By oxidation of inactive fermentation amyl alcohol (Dumas a. Stas, *A.* 33, 156; 35, 143; Erlenmeyer a. Hef, *A.* 160, 267; Pedler, *C.* J. 21, 74).—2. By boiling its nitrile with alcoholic potash (E. a. H.; Schmidt a. Sachtleben, *A.* 193, 87).—3. Together with the active acid by oxidation of leucine (amido-hexolic acid) (E. a. H., cf. Neubauer, *A.* 106, 56).—4. By heating isopropyl-malonic acid at 180° (*B.* 11, 596).—5. By oxidising di-methyl-allyl-carbinol, treating the resulting CMe₂(OH).CH₂CO₂H with HI, and reducing the β -iodo-valeric acid so formed by means of 3 p.c. sodium-amalgam applied in an acid solution (Schirotkoff, *J. pr.* [2] 23, 286).—6. By the action of KOH or HClAq on *Athamantin* (Schneidermann a. Winckler, *A.* 61, 324).—7. By putrefactive fermentation of proteids (Iljenko, *A.* 63, 269).—8. By the action of CrO₃ on gelatin and albumen (Schlieper, *A.* 59, 7; Guckelberger, *A.* 64, 71).—9. From isopropyl-aceto-acetic ether (Frankland a. Duppa, *A.* 145, 84).—10. By distilling isopropyl-malonic acid (Conrad a. Bischoff, *A.* 204, 151).—11. A product of distillation of colophony (Renard, *A. Ch.* [6] 1, 253).

Preparation.—1. **Isoamyl alcohol** is oxidised by less than the calculated quantity of KMnO₄ in the cold. Some acetic acid is formed, but this can be got rid of by distilling a dilute solution of the acids, for valeric acid passes over in the first quarter of the distillate, the acetic acid remaining behind (Duclaux, *C. R.* 105, 171).—2. By oxidising isoamyl alcohol (1,000 c.c.) with K₂Cr₂O₇ (1,000 g.) dissolved in water (3,500 c.c.) by adding in the cold H₂SO₄ (1,400 g.) mixed with water (800 g.). The resulting isoamyl isovalerate is saponified by potash (Pierre a. Puchot, *A. Ch.* [4] 29, 229).—3. By

distilling valerian root with dilute phosphoric acid, neutralising the distillate with Na_2CO_3 , and decomposing the resulting Na^+ salt by H_2SO_4 . In purifying valeric acid use may be made of the fact that the acid forms crystalline acid salts with K and Na (Lescaudr, *Bt.* [2] 27, 104).

Properties.—Liquid, inactive to light. Its smell is powerful and unpleasant. Sol. water. Separated from aqueous solution by CaCl_2 . Volatile with steam. Mixes with alcohol and ether. It is set free from its salts by mineral acids, by HOAc , by oxalic, tartaric, citric, and malic acids, but not by butyric acid. When conc. valeric acid is added to a solution of cupric acetate, anhydrous cupric valerate separates in oily drops, which soon change to a greenish-blue crystalline powder of the hydrated salt; butyric acid would at once give a crystalline pp. (Larocque & Huraut, *J. Ph.* [3] 9, 430).

Reactions.—1. Oxidised by chromic acid mixture at 20° to acetic acid and CO_2 .—2. Boiling dilute HNO_3 forms nitro-valeric acid, methyl-malic acid, and a little di-nitro-propane (when prepared from valerian) or di-nitro-butane (when prepared from isoamyl alcohol) (Bredt, *B.* 14, 1782; 15, 2319; cf. Dessaignes, *A.* 79, 874).—3. Dilute alkaline KMnO_4 forms $\text{CMe}_2(\text{OH})\text{CH}_2\text{CO}_2\text{H}$.—4. Electrolysis of the K salt in 50% solution yields octane C_8H_{18} (Kolbe, *A.* 69, 259).—5. Passed through a red-hot tube it yields ethylene, propylene, butylene, and other hydrocarbons (Hofmann, *C. J.* 3, 121).—6. The Ca salt yields di-isobutyl ketone on distillation by itself, valeric aldehyde on distillation with calcium formate, and methyl isobutyl ketone on distillation with calcium acetate.

Salts.— NH_4A . V. sol. water and alcohol. $(\text{NH}_4)_2\text{H}_2\text{A}$.— KA . Deliquescent crystalline mass. S. (alcohol) 26 at 20° . [140].— LiA . Nodules.— TlA . V. sol. water.— CaA . 8aq. needles (Barone, *A.* 165, 120; Schmidt & Sachtleben, *A.* 193, 87; Schirokoff, *J. pr.* [2] 23, 286). S. 18.4 at 0° (Sedlitzky, *M.* 8, 563).— CaA . 4aq.— CaA . 5aq.— BaA . Triclinic plates. S. 94 at 18° . S. (alcohol) 3.3 at 20° .— BaA . 2aq.— BaA . 2aq.— SrA .— MnA . 2aq.— ZnA . 2aq. Crystalline.— ZnA . S. 1 in the cold. S. (80 p.c. alcohol) 1.7 in the cold; S. (ether) .2 in the cold; .5 at 35° (Witstein, *J.* 1847, 557).— ZnA . 12aq.— ZnA . 8aq.— ZnA . 2 NH_3 (Iutschak, *B.* 5, 30).— CuA . Green crystalline pp.— CuA . 2aq.— BiA . $(\text{OH})_2\text{O}_2$ (Schuchtt, *Ar. Ph.* [3] 2, 97).— FeA .— FeA . $(\text{OH})_2$.— FeA . $(\text{OH})_2$.— PbA . Easily fusible laminae.— PbA . Groups of needles, sl. sol. water.— AgA . S. .177 at 0° (Sedlitzky); .185 at 20° (Erlenmeyer).

Methyl ether MeA . (116°). S.G. 2. 9007. C.E. (0° – 10°) .001174. S.V. 149.6 (Elsässer, *A.* 218, 815); 148.3 (R. Schiff, *A.* 220, 834). S.H. (21° – 45°) .491 (Kopp). Smells like bananas.

Ethyl ether EtA . (134°). (E.). [135° cor.] (Perkin). S.G. 2. 8851 (E.); 8714; 8332 (P.). C.E. (0° – 10°) .001034. S.V. 173.4 (E.); 173.0 (S.). M.M. 7.615 at 18° . Oil, sol. alcohol. Smells like rennet apples and water-mint (Pierre & Puchot, *A. Ch.* [4] 20, 234). Converted by sodium into oxy-decoic acid, ethyl ethoxy-decoate (Hantzsch, *A.* 249,

64), an acid $\text{C}_{10}\text{H}_{18}\text{O}_2$ [c. 127°] (295°), and other bodies (Greiner, *Z.* [2] 2, 460; Wanklyn, *C. J.* 17, 871; Geuther & Greiner, *J.* 1865, 319).

n-Propyl ether PrA . (156°). S.G. 2. 8809. C.E. (0° – 10°) .000997. S.V. 197.5 (Elsässer); 196.8 (Schiff).

Isopropyl ether PrA . (142°). S.G. 2. 870; 854 (Silva, *A.* 153, 136).

Di-chloro-propyl ether $\text{C}_3\text{H}_5\text{Cl}_2\text{A}$. (245°) at 737 mm. S.G. 2. 1.149. Formed from epichlorhydrin and isovaleryl chloride (Truchot, *A.* 138, 298).

Isobutyl ether $\text{C}_4\text{H}_9\text{A}$. (169°) (Elsässer, *A.* 218, 328); (173°) (P. a. P.). S.G. 2. 8736 (E.). 2. 8884 (P. a. P.). C.E. (0° – 10°) .001027. S.V. 223.4 (E.).

Isoamyl ether $\text{C}_5\text{H}_{11}\text{A}$. (188°) (Kopp; R. Schiff, *A.* 234, 344); (196°) (Balard); (190°) (Balbiano, *J.* 1876, 348); (194°) (Kahlbaum). S.G. 2. 870 (Balbiano). S.V. 244.5. V.D. 6.1. Smells, when dissolved in alcohol (7 pts.), like apples.

Octyl ether $\text{C}_8\text{H}_{17}\text{A}$. (250°). S.G. 2. 862 (Zincke, *A.* 152, 6).

Cetyl ether $\text{C}_{18}\text{H}_{37}\text{A}$. (257°). (280°–290°) at 202 mm. S.G. 2. 852 (Dollfus, *A.* 131, 283).

Allyl ether $\text{C}_3\text{H}_5\text{A}$. (154°). Oil (Cahours & Hofmann, *A.* 108, 296).

Glycerol derivative v. Glycerin.
Chloride $\text{Pr.CH}_2\text{COCl}$. (114°) at 726 mm. S.G. 2. 9887. μ_D 1.4213. n_D 1.4914.

Liquid, easily decomposed by water (Béchamp, *C. R.* 42, 224; Brühl, *A.* 203, 24).

Bromide $\text{C}_3\text{H}_5\text{OBr}$. (143°). Liquid.
Iodide $\text{C}_3\text{H}_5\text{OI}$. (168°) (Cahours, *C. R.* 44, 1252).

Anhydride $(\text{C}_5\text{H}_9\text{O})_2\text{O}$. Mol. w. 186. (215°) (Chiozza, *A.* 84, 106). Converted by hydrated BaO into the oily peroxide $(\text{C}_5\text{H}_9\text{O})_2\text{O}_2$ (Brodie, *Pr.* 12, 655).

Aceto-valeric anhydride $(\text{C}_5\text{H}_9\text{O})\text{OAc}$. (147°–160°) (Autenrieth, *B.* 20, 3187).

Amide $\text{C}_5\text{H}_9\text{CONH}_2$. [128°] (Letts, *B.* 5, 669; Hofmann, *B.* 15, 982); [135°] (Schmidt & Sachtleben, *A.* 193, 102). (231°). Silky plates, v. sol. water and alcohol.

Anilide $\text{C}_5\text{H}_9\text{CO.NHPh}$. [115°] (Chiozza, *A. Gb.* [3] 39, 201; Kelbe, *B.* 16, 1200; cf. Dumas, *C. R.* 25, 475, 658; Dessaignes, *A.* 68, 333). Sl. sol. hot water, v. sol. alcohol and ether.

Nitrile $\text{Pr.CH}_2\text{CN}$. **Isobutyl cyanide**. Mol. w. 83. (129°) (R. Schiff, *B.* 12, 587). S.G. 2. 823. V.D. 2.89. Formed by heating ammonium valerate or valeramide with P_2O_5 (Dumas, Malgouti & Leblanc, *C. R.* 25, 558). Occurs among the products of oxidation of gelatin and casein by chromic acid mixture (Schlieper, *A.* 59, 15; Guckelberger, *A.* 64, 72), of the action of chlorine on leucine (Schwaner, *A.* 102, 228), and of the action of conc. HNO_3 on castor oil (Hell & Kitrosky, *B.* 24, 980). Formed also, together with valeramide, by heating valeric acid with potassium sulphoryanide (Letts, *B.* 5, 669). It is also got by the action of cold Ac_2O on the oxim of valeric aldehyde (Dollfus, *B.* 26, 1915). Prepared by digesting isobutyl iodide with KC_y and alcohol, (Erlenmeyer & Hall, *A.* 160, 266). Liquid, smelling like almonds, dissolving in about four times its volume of water

Sodium converts it, on heating, into cyanbutine C_4H_7N , crystallising in stellate groups of needles, which yield $BHCl$ and $B_2H_2PtCl_4$, and is converted by nitrous acid into $C_4H_7(OH)N_2$, [39°] (E. von Meyer, *J. pr.* [2] 37, 407).

Active valeric acid $CHMeEt.CO_2H$. *Methyl-ethyl-acetic acid*. *Hydrotiglic acid*. (177° i.v.). S.G. $\frac{3}{173}$.938 (Saur). S.V. 129.1 (Loesen, A. 254, 60). Occurs in the essential oil from the fruit of *Angelica Archangelica* (R. Müller, *B.* 14, 2476).

Formation.—1. By oxidation of isoamyl alcohol.—2. By reducing tiglic acid with HI and P (Schmidt a. Berendes, A. 191, 117).—3. By heating methyl-ethyl-malonio acid (Bischoff a. Conrad, A. 204, 151).—4. From methyl-ethyl-acetoacetic ether (Saur, A. 188, 257).—5. By reducing angelic acid (Schmidt, A. 208, 261).—6. By reducing bromo-hydro-tiglic acid (Pagensteher, A. 195, 121).—7. By the action of NaOEt and EtI on propionyl-propionic acid (Israel, A. 231, 219).—8. By oxidation of the corresponding aldehyde (Lieben a. Zeisel, M. 7, 56).

Properties.—The acid obtained by synthetic methods is inactive, but when obtained by oxidation of active amyl alcohol it is dextro-rotatory, but is mixed with inactive isovaleric acid. By oxidation of an amyl alcohol $[\alpha]_D = -4.4^\circ$ Guye and Chavanne (*C. R.* 116, 1454) obtained a valeric acid (174°), $[\alpha]_D = +13.6^\circ$, S.G. $\frac{2}{173}$.938. By oxidation of an amyl alcohol $[\alpha]_D = -5.2^\circ$ at 22° Rogers (*C. J.* 63, 1130) got a valeric acid (175°), S.G. $\frac{2}{173}$.936, $[\alpha]_D = +13.9^\circ$ at 22°. Methyl-ethyl-acetic acid can be separated from isopropyl-acetic acid through the greater solubility of its silver salt. Dilute $KMnO_4$ oxidises methyl-ethyl-acetic acid to $CMeEt(OH).CO_2H$.

Salts.— CaA_2 , 5aq: needles. S. (of CaA_2) 1. — BaA_2 : gummy mass. — ZnA_2 : Needles, ore sol. cold than hot water. — CuA_2 : bluish-green, crystalline pp. — AgA_2 : groups of needles. 1:13 at 20° (O. a. B.); 1:11 at 1° (Sedlitzky, M. 8, 668).

Ethyl ether EtA' . (133.5° i.v.). S.G. $\frac{1}{10}$.8695.

Nitrile C_4H_7N . (125°). S.G. 2 .8061. Formed by adding Na and EtI to a solution of acetonitrile in benzene (Hanriot a. Bouveault, *L.* [2] 51, 173). Liquid.

Valeric acid $CM_2.CO_2H$. *Tri-methyl-acetic acid*. [35°]. (163.5° i.v.). S.G. $\frac{2}{105}$.905. β . 2:2 : 20°. **Heat of neutralisation:** Gal a. Werner, *L.* [2] 46, 801. Formed by heating its nitrile with alcoholic potash or conc. H_2SO_4 at 90° (Butleroff, A. 165, 322; 170, 151; 173, 355; 1, 5, 478). Formed also by action of CrO_3 on inapolin (Friedel a. Silva, B. 6, 146, 820) and on tri-methyl-pyruvic acid (Glücksman, M. 20, 77). Monometric crystals. Does not yield a homo-derivative on heating with Br, either alone or in presence of P (Reformatzky, B. 23, 596).

Salts.— NaA , 2aq. Prisms, v. sol. water. — HA' . Needles, m. sol. water. — CaA' , 5aq. — BaA' , 4aq. S. $\frac{1}{10}$ at 1°. — $StrA'$, 5aq. — BaA' , 5aq. — 34 at 2° (Landau, M. 14, 707). — MgA' , 8aq. — ZnA' , 8aq. S. (of ZnA') 1:7 at 20°. The cold saturated solution becomes filled on warming

with a solid salt, which dissolves up again on cooling. — PbA' . — $PbHA'$: needles. — CuA' aq: greenish pp. — AgA' . S. 1:1 at 1°; 1:27 at 27° (Stiasny, M. 13, 599).

Methylether MeA' . (101°) (Butleroff).

Ethyl ether EtA' . (118.5° i.v.). S.G. 2 .875.

Tert-butylether C_4H_9A' . (135° i.v.).

Amyl ether $CM_2.C_4H_9A'$. (165°) (Tissier, *Bl.* [2] 24, 558).

Chloride $CM_2.COCl$. (106°).

Anhydride $(CM_2.CO)_2O$. (190°).

Amide $CM_2.CO.NH_2$. [154°]. (212°).

Formed by heating the ammonium salt in sealed tubes at 230° (Fanchimont a. Klobbie, R. T. C. 6, 238). Long needles. Decomposed by pure HNO_3 (S.G. 1.53; with evolution of N_2O).

Methylamide $CM_2.CO.NHMe$. [91°]. (204°).

Dimethylamide $CM_2.CO.NHMe_2$. (186°).

Ethylamide $CM_2.CO.NHEt$. [49°]. (204°).

Diethylamide $CM_2.CO.NEt_2$. (203°). S.G. 13 .891.

Nitrile $CM_2.CN$. *Tert-butyl cyanide*. [16°]. (106°). Formed, together with a polymeride (160°), by the action of tert-butyl iodide on dry potassio-mercuric cyanide below 5° (Butleroff, A. 170, 151; Freund a. Lenze, B. 23, 2866; 24, 2161). Crystalline mass with pungent smell. On heating with aniline hydrochloride it yields phenyl-valeramide, which forms an oxalate [192°]. Hydroxylamine forms the amidoxim $CM_2.C(NH_2).NOH$ [116°].

References.—AMIDRO, BROMO, CHLORO-, IODO-, NITRO-, NITROSO-, AND OXY-VALERIC ACIDS.

n-VALERIC ALDEHYDE

$CH_3.CH_2.CH_2.CH_2.CHO$. (103°) S.G. 11 .819. Formed by distilling calcium n-valerate with calcium formate (Lieben a. Rossi, A. 159, 70; Zander, A. 224, 81).

Isovaleric aldehyde $(CH_3)_2CH.CH_2.CHO$.

Valeral. Mol. wt. 86. (92.5°). S.G. $\frac{1}{10}$.8041; 2° .7951 (Perkin, C. J. 45, 477). μ . 1.8934. n_D^{20} 40.66 (Brühl). V.D. 43.06 (calc. 43) (Schröder, B. 4, 400, 468). S.V. 118.5. Formed by oxidation of isoamyl alcohol (Dumas a. Stas, A. Ch. [2] 73, 145; Parkinson, A. 90, 114; Kolbe a. Guthrie, A. 109, 296). Formed also by distilling calcium iso-valerate with calcium formate (Lamprecht, A. 97, 370), by the distillation of iso-valerates (Chancel, A. 60, 318; Ebersbach, A. 106, 262; Schmidt, B. 5, 600), by oxidation of gluten (Keller, A. 72, 84) and castor oil (Arzbücher, A. 73, 202), and by the action of SO_2 on leucine (Schwanert, A. 102, 226).

Properties.—Neutral oil, with pungent fruity odour. Polymerises on keeping. Mixes with alcohol and ether. On heating with ammonium sulphocyanide it yields a dark-red liquid, sol. alcohol, ether, and HOAc (Broday, M. 8, 87). Alkaline sodium nitroprusside gives a violet-red colour, destroyed by HOAc (Von Ertlo, A. 267, 876). Combines with sodium bisulphite, forming $(O_2H_2O)NaHSO_3$.

Reactions.—1. Readily oxidised to valeric acid.—2. Chlorine forms mono- and di-chloro-valeric aldehydes, and, at 140°, oily $C_5H_9Cl_2O$ (204°), which is converted by alcoholic soda into $C_5H_9Cl_2O$ (209°).—3. PCl_5 forms $C_5H_9Cl_2O$.—4. Potash-fusion gives valeric acid.—5. Heating with lime forms isoamyl alcohol, calcium

valerate and other bodies (Fittig, *A.* 117, 68).—6. *Sodium-amalgam* and water slowly form isoamyl alcohol (Wurtz, *Z.* 134, 201).—7. *Sodium* forms isoamyl alcohol, sodium valerate, decyl alcohol $C_{10}H_{20}O$ (203°), an oil $(C_8H_{16}O)_n$ (260°–290°), the compound $C_{10}H_{18}O_2$, and the acid $C_8H_{16}O_2$ (Borodin, *Z.* 1864, 353; *E.* 5, 480).—8. KOH at 0° produces an oily polymeride, lighter than water, not capable of combining with $NaHSO_4$, and yielding isovaleric aldehyde and the compounds $C_{10}H_{18}O$ and $C_{10}H_{16}O_2$ on distillation (Borodin, *B.* 6, 982). This polymeride, left in contact with Na_2CO_3 aq., often forms needles of $C_{10}H_{16}O_2$ [70°].—9. Heating with KOH forms the aldehyde $C_{10}H_{18}O$ and a compound $C_{10}H_{16}O_2$ (260°–290°). S.G. .90.—10. Heating with *zinc* at 180° forms decenoic aldehyde $C_{10}H_{18}O$ (190°), S.G. .2 .862 (Riban, *C. R.* 75, 96; Kekulé, *A.* 162, 77) and other products.—11. *ZnEt*, produces the oil $(C_8H_{16}O)_n$, in large quantity (Beilstein, *A.* Rieth, *A.* 126, 242). *ZnMe*, followed by water, forms mekyl-isobutylcarbinol (Kuvsinoff, *J. R.* 1887, 204).—12. Dry K_2CO_3 at 50° forms an oily polymeride, which is reconverted at 180° into the aldehyde. Boiling with K_2CO_3 yields $C_{10}H_{18}O$ (*v. supra*), $C_{10}H_{16}O_2$ (265°–270°), and $C_{10}H_{14}O_2$ (235°–240°) (Gäss, *A.* Hell, *B.* 8, 369).—13. Dry K_2CO_3 added to moist isovaleric aldehyde forms, after some days, crystals of a polymeride [84°], which is reconverted at 108° into the original aldehyde (Bruylants, *B.* 8, 414).—14. PH_3I forms a compound $(C_8H_{16}O)_nPH_3I$, crystallising from ether in plates [119°], converted by cold potash into $(C_8H_{16}O)_nPH_3OH$, crystallising in prisms [125°], insol. water (De Girard, *A. Ch.* [6] 2, 33; *C. R.* 94, 215).—15. On heating with *hydrophosphoric acid* in an atmosphere of hydrogen the compound $(C_8H_{16}O)_nH_3PO_4$ [160°] is formed. It yields BaA_2 aq (Ville, *C. R.* 109, 71).—16. $AcCl$ at 100° combines, forming chloro-amyl acetate $C_8H_{17}CH_2CO_2Ac$ (Maxwell Simpson, *Pr.* 27, 120).—17. *m-Amido-benzoic acid* forms $C_{10}H_{17}NO$, [c. 430°].—18. Dry HCl forms $(C_8H_{17}CH_2Cl)_nO$ (180°) (Bruylants, *B.* 8, 414).—19. Conc. NH_3 aq forms isovaleric aldehyde-ammonia $C_8H_{17}CH(NH_2)OH$ 7aq [58°] (Erdmann, *A.* 130, 211; Petersen, *A.* 132, 158; Ljubavin, *B.* 6, 1460), which yields, on allowing its alcoholic solution to stand, or on boiling with potash, the oily 'trioxymylamine' $C_8H_{17}NO_3$, forming $BHCl$ [113°] and $B_2H_2PtCl_6$. $AgNO_3$ reacts with isovaleric aldehyde-ammonia, forming $(C_8H_{17}N)_3AgNO_3$ and $(C_8H_{17}N)_3AgNO_3$ (Goldschmidt, *B.* 11, 1200; Mixter, *J.* 1878, 438).—20. Alcoholic NH_3 at 150° forms valeritrine, hydrovaleritrine, and other bodies. Valeritrine $C_{10}H_{18}N$ is a very unstable liquid (250°–260°), yielding BH_2HgCl_2 [88°], $B_2H_2PtCl_6$, and $B_2C_8H_{16}N_2O$ [130°]. Hydrovaleritrine $C_{10}H_{18}N$ or $C_{10}H_{17}N$ is a liquid, yielding crystalline $BHCl$, S. 2-87 at 22°, not melted at 180° (Ljubavin, *B.* 8, 565).—21. H_2S passed into an aqueous solution forms thiovaleric aldehyde $C_8H_{17}S$ (89°). An isomeride (115°) is got, together with a polymeride [94-5°], by heating isovaleric aldehyde with sulphur at 250° (Barbaglia, *B.* 13, 1574; 17, 2654; *G.* 11, 95, 16, 426).—22. CS_2 and NH_3 aq form carbovaleraldine $C_{10}H_{18}N_2S_2$ (Schröder, *B.* 4, 469; Mulder, *A.* 168, 237), which melts at 109°

(Guareschi, *A.* 222, 811).—23. $NH_3CS.OEt$ and HCl form $C_8H_{17}(NH_3CS.OEt)$, [108°] (Bischoff, *B.* 7, 1078).—24. H_2Se passed into an aqueous solution of valeric aldehyde forms $C_8H_{17}Se$ [56-5°].—25. *Acetone* and dilute $NaOH$ yield $Pr.CH_2CH.CO.CH.CO.CH$, (180°) (Barbier, *A.* Bouveault, *C. R.* 118, 198).

Oxim $C_8H_{17}CH:NOH$. Mol. w. 101. (163°). S.G. .8934 (*in vacuo*); μ_n 1.487 (Petraczek, *B.* 16, 829; Trapezonzjan, *B.* 26, 1428). It is a *syn*-oxim, because it yields valeritritrile when mixed with Ac_2O and ether (Dollfus, *B.* 25, 1915).

Isovaleric orthaldehyde. *Amylidene glycol*. *Acetyl derivative* $C_8H_{17}CH(OAc)_2$. (195°). Formed by heating isovaleric aldehyde with Ac_2O at 200°.

Benzoyl derivative $C_8H_{17}CH(OBz)_2$. [111°]. (264°). Formed by heating the aldehyde with Bz_2O at 260° (Guthrie & Kolbe, *A.* 109, 298).

Di-methyl ether $C_8H_{17}CH(OMe)_2$. (124°). S.G. .852. Formed from isovaleric aldehyde (2 vols.), $MeOH$ (5 vols.), and $HOAc$ (1 vol.) (Alsborg, *J.* 1864, 486).

Di-ethyl ether $C_8H_{17}CH(OEt)_2$. (168°). S.G. .835. Formed in like manner.

Di-isomyl ether $C_8H_{17}CH(OC_4H_9)_2$. (c. 248°). S.G. .849.

Ethyl isomyl ether $C_8H_{17}CH(OEt)(OC_4H_9)$. (c. 205°). S.G. .875. Formed by the action of Na on an ethereal solution of isovaleric ether (Greiner, *Z.* 1866, 465).

Valeric aldehyde $CHMeEt.CHO$. (91°). Formed by reducing tiglic aldehyde with iron and $HOAc$ (Herzig, *M.* 8, 123; Lieben & Zeisel, *M.* 7, 56), and by warming $CH_2CH.CHEt.OH$ with dilute (1 p.c.) H_2SO_4 (Kondakoff, *J. R.* 20, 154).

Valeric aldehyde $CMe_2.CHO$. [83°]. (75°). S.G. .7927 (Tissier, *Bl.* [2] 24, 558).

Di-isovaleric aldehyde v. DECENOIC ALDEHYDE.

Reference.—DI-BROMO-, CHLORO-, IODO-, and OXY-VALERIC ALDEHYDE.

VALEROGUANAMINE $C_8H_{17}N_3$, *i.e.*

$PrCH_2.CN.N.C(NH) > NH$. *Butylguanamine*.

[173°]. Formed by heating guanidine isovalerate (Bandrowski, *B.* 9, 240; Haaf, *J. pr.* [2] 43, 76). Flat plates (from water). Weak base.— $BHCl$: needles, v. sol. water.— $B_2H_2SO_4$.— B_2AgNO_3 .

VALEROLACTIDE v. OXY-VALERIC ACID.

VALEROLACTONE v. OXY-VALERIC ACID.

VALERONE v. DI-ISOBUTYL KETONE.

VALERONITRILE v. Nitrile of VALERIC ACID.

VALEROVALERIC ACID v. VALERYL-VALERIC ACID.

DIVALERYL $C_{10}H_{18}O_2$, *i.e.* $C_8H_{17}.CO.CO.C_8H_{17}$. (270°–280°). Formed by the action of N_2 on valeryl chloride (Brühl, *B.* 12, 315). Oil.

VALERYL-ACETOPHENONE v. PHENYL-BUTYL METHYLENE KETONE.

VALERYL CHLORIDE v. Chloride of VALERIC ACID.

VALERYL-CYANAMIDE v. CYANIC ACIDS.

VALERYLENE v. PENTYNE and also BROMO- and DI-CHLORO-VALERYLENE.

VALERYLENE TETRABROMIDE v. TETRABROMO-PENTANE.

VALERYLENE HYDRATE v. PENTENYL ALCOHOL.

VALERYLENE HYDROCHLORIDE g. CHLORO-AMYLENE.

VALERYL-VALERIC ACID. *Ethyl ether* $C_{12}H_{20}O_4$, i.e. $CH_3Pr.CO.CHPr.CO_2Et$. (206°) at 722 mm. Formed by the action of sodium on isovaleric ether (Greiner, *Z.* 1866, 461; Wohlbruck, *B.* 20, 2335). Oil, sol. alcohol and ether.

VALYLENE C_8H_8 . Mol. w. 66. (50°). A product of the action of alcoholic potash on valerylène dibromide (Reboul, *A.* 135, 372). Liquid, with odour of garlic and prussic acid. Ammoniacal $CuCl_2$ ppt. yellow C_8H_8Cu , which yields the pure hydrocarbon on treatment with dilute $HClAq$. Bromine at 0° forms crystalline $C_8H_8Br_2$. Ammoniacal $AgNO_3$ yields a white pp. of C_8H_8Ag .

VANADATES v. VANADIUM OXYACIDS, AND SALTS AND DERIVATIVES THEREOF, p. 851.

VANADIC ACIDS v. VANADIUM OXYACIDS, p. 851.

VANADIUM. V . At. w. 51.2. Mol. w. not known. Melts at a very high temperature; probably higher than m.p. of Mo, which does not melt at 1700°–1800° (Moissan, *C. R.* 116, 1225). S.G. 5.5 at 15° (Roscoe, *T.* 1869, 679). For emission-spectrum, obtained by using electric sparks, v. Thalén (*A. C.* [4] 18, 243).

Historical.—In 1801 Del Rio announced the discovery of a new metal in a lead ore from Zimapán in Mexico (*C. A.* 71, 7); to this metal he gave the name *erythronium*, but at a later time he thought the metal was only impure chromium. In 1830 Sefström found a new element in the bar-iron and refinery slags where iron-ore from Taberg in Sweden was smelted (*P.* 21, 43); this element he called *vanadium* (from a Scandinavian deity *Vanadis*). In the same year (*P.* 21, 49) Wöhler found that the lead ore examined in 1801 by Del Rio contained lead vanadate; and he showed that the metal which Del Rio had called erythronium, and had then supposed to be impure chromium, was really vanadium. In 1831 Berzelius supposed he had prepared vanadium by heating an oxychloride of NH_4 , and also by heating the highest oxide with K (*P.* 22, 1); but in 1867 Roscoe (*T.* 1869, 1; 1869, 679; v. also 1870, 317) showed that one of the substances which until then had been taken to be the element V was a nitride, and that another substance, taken to be V , was an oxide of this element. Roscoe obtained pure V by heating VCl_3 to redness for many hours in dry H . Roscoe was led to doubt the accuracy of the statement of the properties and at. w. of V that had been accepted on the authority of Berzelius, because he found that several compounds of V and Pb were isomorphous, but that it was impossible to assign comparable formulae to these compounds if the at. w. given by Berzelius for V were accepted (v. *T.* 1868, 1 *et seq.*). Berzelius gave the value 68.5 to the at. w. of V ; he assigned the formulae VO , VO_2 , and VO_3 ($O_2=8$) to the three oxides, and classed V with Cr , Mo , and W . Roscoe's researches showed that the at. w. of the metal is 51.2, that the oxides are best represented as V_2O_3 , V_2O_5 , and V_2O_6 , that the substance thought to be V , was

really chiefly V_2O_5 , that the compound supposed by Berzelius to be VCl_3 was $VOCl_3$, and that V must be classed with Pb and As .

Occurrences.—Small quantities of compounds of V are found fairly widely distributed; the element does not occur uncombined. The chief minerals that contain V compounds are *mottramite* ($Cu-Pb$ vanadate), *descloisite* ($Pb-Zn$ vanadate), *dechenite* ($Pb-Zn-Cu$ vanadate), *roscoelite* (Al vanadate with K silicate), *vanadinite* (vanadate of lead with lead chloride), and some other minerals, which generally contain vanadates of Cu , Pb , Zn , or Ca . Small quantities of compounds of V are found in all *pisolitic limonites* (Böttger, *C. C.* 1873, 514), in some *pitchblendes*, *clays*, and *basalts*, and in a few other rocks. Compounds of V have also been found, in small quantities, in the slag from copper extraction works (Karsten, *P.* 52, 629; Witz u. Osmond, *Bl.* [2] 38, 49); in many specimens of pig-iron (v. Riley, *C. J.* 17, 21; cf. Hodges, *C. N.* 26, 238; Walz, *Am. Ch.* 6, 453); in some meteorites (v. Apjohn, *C. J.* 27, 104); in caustic soda and sodium phosphate (Schöne a. Rahmelsberg, *B. B.* 1864, 681; Donath, *D. P. J.* 240, 318); and, according to Lookyer (*Pr.* 27, 279), probably in the sun.

Preparation.—1. From the refinery slag of the Taberg iron-ore. The finely-powdered slag is heated with KNO_3 and Na_2CO_3 , the fused substance is digested with boiling water, and solution of a salt of Ba or Pb is added to the filtered liquid; the ppd. Ba or Pb vanadate is decomposed by boiling with a slight excess of H_2SO_4 , and the solution is filtered from $BaSO_4$ or $PbSO_4$; the filtrate is neutralised by NH_4Aq and concentrated, and pieces of NH_4Cl are placed in the liquid until some NH_4Cl remains undissolved; the NH_4VO_3 , which is thus ppd. as a white crystalline powder is washed with conc. NH_4ClAq , and then with alcohol, and is then decomposed by heating strongly in an open vessel, whereby V_2O_5 is produced (Berzelius, *P.* 22, 1). Wöhler (*A.* 78, 125) employed a very similar process for preparing V_2O_5 from *limonite*.—2. From vanadinite. L'Hôte (*C. R.* 101, 1151) recommends to mix finely-powdered *vanadinite* (approximately $3Pb_3V_2O_7 \cdot PbCl_2$) with four times its weight of lampblack and a little oil, to heat strongly in a closed vessel, and then to heat to 300° in a stream of dry Cl_2 , whereby $VOCl_3$ is formed, and distilled over into a cooled U-tube; other compounds of V are readily prepared from $VOCl_3$.—3. From the cobalt-ore of Mottram in Cheshire. This source of V compounds was discovered by Roscoe (v. *C. J.* [2] 6, 326). The Cheshire Keuper sandstone contains carbonates of Cu , carbonate of Pb and *galena*, *black cobalt-ochre*, iron oxides, and salts of As , Ag , Mn , and Ba . The compound of V was probably *vanadinite*. The sandstone was crushed, and the metallic compounds were dissolved by $HClAq$; bleaching-powder and milk of lime were added till the reaction was alkaline; and it was from the pp. thus obtained that Roscoe prepared V and its compounds. The lime pp. contained chiefly As , Cu , Fe , Pb , V , and Ca in combination with SO_4 and PO_4 ; it was heated in a furnace with ground coal to remove As , then roasted with a quarter its weight of Na_2CO_3 ,

and lixiviated with water; the solution was saturated with H_2S and filtered, and H_2S was boiled off; crude oxide of V was then pptd. by NH_4Aq ; the oxide was dried and heated with conc. HNO_3Aq to oxidise it to vanadic acid, which was then boiled with saturated $(NH_4)_2CO_3Aq$, and the somewhat soluble NH_4 vanadate was crystallised from water, and then strongly heated in an open vessel; the V_2O_5 thus obtained was suspended in water into which NH_3 was passed; the solution of NH_4 vanadate was filtered from silica, phosphates, &c., evaporated to dryness, and heated in an open vessel until V_2O_5 remained.

The metal vanadium is prepared by reducing VCl_3 in H (for preparation of VCl_3 , *v. VANADIUM DICHLORIDE*, p. 844). The process is conducted in perfectly pure and dry H; every trace of moisture and air must be excluded. The pure and dry H is passed for 12 hours through a porcelain tube, connected (by specially arranged paraffin-joints) by a glass tube, to the H apparatus; the VCl_3 is then placed in the porcelain tube (a special arrangement for doing this is described by Roscoe), and H is passed through the apparatus for 6 hours. The porcelain tube is then gradually heated to full redness, and the passage of H is continued so long as HCl is given off, after which the tube is allowed to cool for several hours in the stream of H. The process occupies from 40 to 80 hours according as from 1 to 4 g. of VCl_3 are used. The V thus obtained contains traces of H and O. Reduction proceeds more quickly at a white heat, but the product is not so pure; it generally contains c. 85 to 96 p.c. V. (For details, and figures of the apparatus, *v. Roscoe*, *T.* 1869. 679; 1870. 317; or *C. J.* [2] 8, 344; 9, 23.)

Moissan (*C. R.* 116, 1225) obtained V containing from 17.5 to 25.7 p.c. C, by heating a mixture of C and one of the oxides of V in an electric furnace, using a current of 70 volts and 1,000 amperes; with a current of 70 volts and 850 amperes reduction proceeded very slowly.

Vanadium, mixed with V_2O_5 , was obtained by Roscoe (*l.c.*) by strongly heating a mixture of one of the chlorides of V with Na in an atmosphere of H, and lixiviating with water; the admixed black, powdery V_2O_5 can be removed from the heavier, grey, lustrous, metallic powder, by repeated washings with water, and a substance containing c. 91 p.c. V can be obtained.

The substance supposed by Berzelius (*P.* 22, 1) to be V, and obtained by heating V_2O_5 with K, was shown by Roscoe to consist chiefly of V_2O_5 . The black powder which Uhrlaub (*F.* 103, 134) prepared by heating V oxychloride in NH_3 , and which he supposed to be V, was found by Scharfrik (*W. A. B.* 38, 5) to be VN_3 (*cf. Roscoe, l.c.*).

Properties.—A light-grey, lustrous powder; under the microscope it is seen to be composed of crystalline, silver-white particles. Does not become coherent and dense when strongly compressed. S.G. 5.5 at 15° . Not magnetic. Is not oxidised in air at the ordinary temperature, nor by moistening and then drying *in vacuo*. Has not been melted, except perhaps when reduced from the oxides by C in an electric furnace (*v. Moissan, C. R.* 116, 1225). When powdered V is thrown into a Bunsen flame it burns brilliantly; when strongly heated in O it forms

V_2O_5 ; and when slowly heated in air it perhaps forms V_2O_4 , then V_2O_3 , V_2O_2 , and finally V_2O . Burns in Cl, forming VCl_3 ; combines with N to form VN; also combines with S. V is insoluble in $HClAq$; it dissolves in hot conc. H_2SO_4 and in HNO_3Aq . V dissolves in molten NaOH, giving off H, and forming δ vanadate. V acts on glass vessels in which it is heated, forming a compound with Si; it also alloys with Pt (*B., l.c.*).

The at. w. of V has been determined (1) by reducing V_2O_5 to V_2O_3 by heating in H (Berzelius, *P.* 22, 15 [1831]; Roscoe, *T.* 1868. 8); (2) by oxidising V_2O_3 to V_2O_5 by HNO_3 (*B., l.c.* [1831]); (3) by analysing $(V_2O_5)(SO_4)_2 \cdot 4H_2O$ (*B., l.c.*, p. 18 [1831]); (4) by ppg. $VOCl_3$ by $AgNO_3Aq$, removing excess of Ag from the filtrate, evaporating to dryness, heating, and weighing the V_2O_5 produced (*B., l.c.* [1831]); (5) by determining the weight of Ag required to ppt. the Cl from $VOCl_3$; also by weighing the $AgCl$ ppt.; also by filtering from $AgCl$, evaporating, and weighing the V_2O_5 obtained (Roscoe, *T.* 1868. 23); (6) by determining V.D.s of, and analysing, VCl_3 and $VOCl_3$ (*g. v.*). The results obtained by Berzelius (with the necessary corrections on account of the wrong formulae used by him; *v. Roscoe, l.c.*) gave values for at. w. of V varying from 49.3 to 52.5; Roscoe's values from the reduction of V_2O_5 to V_2O_3 varied from 51.13 to 51.55, and from the analyses of $VOCl_3$ from 50.32 to 51.877. The S.H. of V has not been determined.

Vanadium is both metallic and non-metallic in its reactions. V_2O_5 interacts with strong acids to form divanadyl salts, $V_2O_5(SO_4)_2$, &c.; hypovanadates $V_2O_5(OM)_2$ are also derived from a hydrate of V_2O_5 ; V_2O_5 interacts with conc. H_2SO_4 to form $V_2O_5 \cdot 3SO_3$ and $V_2O_5 \cdot 2SO_3 \cdot xH_2O$; V_2O_5 also forms $V_2O_5 \cdot H_2O$ ($=HVO_3$) and $V_2O_5 \cdot 2H_2O$ ($=H_2V_2O_7$), which react as acids, and salts of the acid HVO_3 are also known; V_2O_5 also combines with various acidic oxides (P_2O_5 , MoO_3 , &c.) and basic oxides, to form complex, salt-like compounds. The sulphides of V dissolve in alkali sulphide solutions; several thiovanadates have been isolated, *e.g.* $(NH_4)_2VS_4$; and also thio-oxyvanadates, *e.g.* $Na_2VS_2O_6$. The haloid compounds of V are generally decomposed by water to oxyhaloid compounds.

Vanadium is placed in Group V., with N, P, As, Nb, Sb, Bi, Er, Ta and Bi. V is the second member of the even series family of this group, the family consisting of N, V, Nb, Ta and an unknown element with an at. w. between those of Th (=232) and U (=239). Group V does not show a marked division into families; the gradation of properties from N to Bi is fairly regular, nevertheless the families (1) N and P, (2) V, Nb and Ta, (3) As, Sb and Bi are distinctly indicated. No hydrides of members of the vanadium family have been isolated with certainty. The highest oxides, M_2O_5 , are salt-forming; all of them interact with alkalis to form salts containing the elements M in the acidic radicles; V_2O_5 also forms basic salts $(VO)_2R_2$, with strong acids; normal salts have not been obtained by the reactions of M_2O_5 with acids. Oxyacids of V, viz. HVO_3 and $H_2V_2O_7$, have been isolated, but definite oxyacids of Nb and Ta are unknown. Both Nb and Ta form chlorides, corresponding with their highest

oxides M_2O_3 ; but the highest haloid compound of V is VX_5 , corresponding with V_2O_5 ; oxyhaloid compounds of V of the form of VX_3 exist ($VOCl_3$, $VOBr_3$) (v. NITROGEN GROUP OF ELEMENTS, vol. iii. p. 671).

In considering the relations between vanadium and the elements of Group V, the position of V in series 4 must be taken into account: as compared with the elements that form series 3, in which series P is placed, the elements of the vanadium series are metallic (V is preceded by Ti, Sc, Ca and K, and is followed by Cr, Mn, and the iron elements); the elements of the vanadium series are nearly as metallic, and also as non-metallic, as Rb, Sr, Y, Nb, Mo, —, and the Ru metals, which elements form series 6, i.e. the niobium series. Hence V would be expected to be distinctly more like a metal, in its chemical relations, than P, and about equal to Nb in its metallic and non-metallic tendencies. As V is the second member of the even series family of Group V., it might be expected to resemble N, which is the first of the even series elements of this group; but it is to be remembered that the differences between the first and second even series members of the groups (i.e. the differences between Li and K, Be and Ca, B and Sc, C and Ti, N and V, O and Cr, F and Mn), become more marked in passing from Group I. to Group VII., and it is also to be remembered that the resemblances between the first even series members and the succeeding odd series members, become more marked as the atomic weights increase; F is more like Cl and Br than O is like S, Se, and Te; but O resembles S, Se, and Te more than N resembles P, As, Sb, &c.; and C is more like Si, Ge, Sn, &c., than B is like Al, Ga, In, &c.; and C less resembles Si, &c., than N resembles P, &c.

Reactions and Combinations.—(Roscoe, *T.* 1869. 679; 1870. 317.) 1. Heated in air, V burns to V_2O_5 ; lower oxides are first formed if the temperature is low.—2. Does not decompose water at 100° .—3. Heated to redness in chlorine burns to VCl_5 ; heated in bromine produces VBr_3 ; does not combine with iodine.—4. Heated with excess of sulphur, V forms V_2S_3 (v. Kay, *C. J.* 37, 728).—5. Heating in a stream of pure nitrogen produces VN.—6. V combines directly with silicon and also with platinum.—7. Mollen potash or soda dissolves V, forming an alkali vanadate and giving off H.—8. V dissolves in conc. sulphuric acid (? forming a vanadyl salt); also in nitric acid, probably forming a basic nitrate; also, slowly, in hydrofluoric acid (? forming VF₃).

Detection and Estimation.—Small quantities of compounds of V give a colorless borax or microcosmic salt bead in the outer flame, becoming green in the reducing flame; if much V compound is present the bead is yellow in the outer flame. Solutions of V_2O_5 in acids are not pptd. by H_2S , but are reduced to solutions of V_2O_3 , which are lavender-blue; if reduction is effected by Zn, Cd, or Na-amalgam the liquid becomes green, then blue, and finally lavender-blue; after reduction the solution bleaches indigo very rapidly, and soon absorbs O. Solutions of vanadates, either neutral or acidified by acetic acid, give finely-divided black pps. with tincture of galls, and the liquids appear like ink.

When an acidified solution of a vanadate is shaken with an ethereal solution of H_2O_2 , the latter solution becomes dark red (Werther, *J. pr.* 88, 195).

Vanadium is generally estimated by converting it into an ammonium salt, strongly heating this in air, and either weighing the V_2O_5 thus produced or heating in H and weighing the V_2O_3 that remains. For a volumetric method of estimating V^{vo}, Gerlach (*B.* 10, 1216).

Vanadium, acids of, v. VANADIUM OXYACIDS, AND SALTS, AND DERIVATIVES THEREOF, p. 851.

Vanadium, bromides of. Only one bromide of V has been obtained.

VANADIUM TRIBROMIDE VBr_3 . Mol. w. not known; from analogy of PBr_3 , $AsBr_3$, &c., the formula VBr_3 is probably molecular. Formed by heating V or VN to redness in vapour of Br. Also by passing Br vapour over a mixture of V_2O_5 and C kept at a red heat; $VOBr_3$ is formed, then $VOBr_2$, and then VBr_3 sublimes (Roscoe, *T.* 1870. 317). Roscoe (*l.c.*) recommends to prepare VBr_3 by placing pure VN in a porcelain boat in a tube of hard glass, driving out all air by dry CO_2 , then passing vapour of Br through the tube while that part where the boat is placed is heated to redness, when brown vapours are given off and condense on the cooler parts of the tube, and finally driving out all traces of Br by a stream of dry CO_2 . VBr_3 is a greyish black, opaque, amorphous, very deliquescent solid; loses Br even in a sealed tube; heated gently in air gives V_2O_5 , and at a higher temperature V_2O_3 . Dissolves in water, without giving off any Br, forming a brown liquid which goes green on addition of a few drops of $HClAq$; this reaction is said by R. to be characteristic of a salt of V_2O_5 .

Vanadium, chlorides of. Three chlorides have been isolated: VCl_5 , VCl_4 , and VCl_3 . V burns when heated in Cl_2 , forming VCl_5 , and the other chlorides are formed by reducing VCl_5 by H. The V.D. of VCl_5 has been determined, and the formula VCl_5 is molecular; the formula VCl_3 is probably molecular, from the analogy of $AsCl_3$, PCl_3 , $BiCl_3$, &c.; VCl_4 , AsI_3 , PI_3 and $BiCl_3$ are the only haloid compounds of the form MX_3 that have been isolated in Group V.; the mol. w.s. of these compounds have not been determined.

VANADIUM TETRACHLORIDE VCl_4 . Mol. w. 192.68. Prepared by Roscoe (*T.* 1869. 691).

Formation.—1. V or VN is heated in Cl_2 .—2. The vapour of $VOCl_3$, mixed with excess of Cl_2 , is passed slowly over a long layer of sugar-charcoal heated to redness.

Preparation.—VN is heated to redness in a tube of hard glass, in a current of pure, dry Cl_2 , which must be free from air. The first few drops of distillate are rejected, as they contain traces of $VOCl_3$ formed from traces of oxide in the nitride used. The dark-red liquid that is formed is saturated with dry Cl_2 , then heated for some hours in a current of dry CO_2 in a vessel connected with an upright condenser, and then fractionated.

Properties and Reactions.—A thick, dark, brownish-red liquid; boils at 154° under 760 mm. pressure. S.G. 1.8584 at 0° , 1.8863 at 8° , 1.8169 at 30° . V.D. 98.1 at c. 200° . Does not solidify at any temperature above -18° . Slowly decomposes to VCl_3 and Cl_2 at ordinary temper-

tures, more quickly when exposed to light, and rapidly when heated. Gives off white fumes in the air. Dissolves in water, forming a blue solution, which does not bleach; this solution is oxidised by KMnO_4 to HClO_4 and V_2O_5 . 2VCl_3 taking up O. Reacts violently with alcohol and ether, forming deep-coloured liquids. When heated with Br in a sealed tube, VCl_3 is formed. VCl_3 does not combine with Cl to form a higher chloride. H_2S reacts with VCl_3 to form VCl_2 , HCl , and S (Kay, *C. J.* 38, 736).

VANADIUM TRICHLORIDE VCl_3 . Mol. wt. not determined, but formula is probably molecular from analogy of PCl_3 , AsCl_3 , &c. Prepared by heating VCl_3 in a retort as long as Cl is given off, and heating the residual solid to 160° in a stream of dry CO_2 (Roscoe, *T.* 1869, 691). Also by heating pure V_2S_5 in a stream of dry, air-free Cl, separating S_2Cl_2 by repeatedly distilling the liquid product, and heating the residue at 140° in dry CO_2 to remove the last traces of S_2Cl_2 (Halberstadt, *B. f.* 1619). Lustrous, peach-blossom coloured tablets, resembling CrCl_3 ; S.G. 8.0 at 18° . Deliquesces very rapidly in air to a brown liquid, which goes green on addition of a drop or two of HClO_4 ; this solution is oxidised by KMnO_4 . 2VCl_3 taking up 2O, to HClO_4 and V_2O_5 . Soluble in alcohol and in ether. Heated in air forms V_2O_5 . Heated in H is reduced to VCl_2 , and then, gradually, to V.

VANADIUM DICHLORIDE VCl_2 . Mol. w. not known. Formula possibly VCl_2 . Prepared by passing vapour of VCl_3 , mixed with a large excess of pure, dry H, through a glass tube heated to dull redness. The distillation of VCl_3 should be slow, and the mixture of vapour of VCl_3 and H should be brought at once into the heated part of the tube. Forms apple-green, micaceous, hexagonal plates; S.G. 8.23 at 18° ; very hygroscopic. Dissolves in water, forming a violet solution, which bleaches indigo and litmus, and reacts as a solution of a salt of V_2O_5 . Dissolves in alcohol and in ether. The solution in water is oxidised by KMnO_4 to HClO_4 and V_2O_5 . 2VCl_2 taking up 3O. Heated in H, is slowly reduced to V; heating to whiteness in NH_3 produces VN (Roscoe, *l.c.*).

Vanadium, ferrocyanide of, v. vol. ii. p. 337.

Vanadium, fluorides of. Only one fluoride, VF_3 , has been isolated; there are indications of the existence of a higher fluoride in solutions in conc. HFAg .

VANADIUM TRIFLUORIDE $\text{VF}_3 \cdot 3\text{H}_2\text{O}$. Mol. w. not known; formula probably molecular, from analogy of trihalides of other elements of Group V. Prepared by evaporating a solution of V_2O_5 in HFAg at 100° , and crystallising from water containing a little HFAg . A white crystalline crust, consisting of rhombohedra. Easily soluble in water; solution reacts acid. Insoluble in conc. alcohol. Effloresces in air; loses some water at 106° , and all at 130° , with absorption of O; V_2O_5 is formed on heating to redness in air. An aqueous solution reduces Ag salts to Ag, Hg and Cu salts to mercurous and cuprous salts; all acids or alkali carbonates ppt. $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ from VF_3 (E. Petersen, *J. pr.* [2] 40, 44).

Vanadoxyfluorides. (Fluovandates.) A number of compounds of the forms $\text{VF}_3 \cdot x\text{MF}$ and $\text{VF}_3 \cdot x\text{M}^n\text{F}$ were obtained by Petersen (*l.c.*) by adding various fluorides to solutions of V_2O_5 .

in HFAg , and crystallising. These salts are generally greenish coloured, and crystalline; most of them are soluble in water, but not in KFAg ; they lose water of crystallisation from 100° to 200° . The vanadoxyfluorides may be regarded as salts of hypothetical acids HVF_3 , H_2VF_4 , and H_3VF_5 ; they may also be formulated as double salts (*q. supra*). The following salts are described by Petersen (*l.c.*):

Ammonium vanadoxyfluorides $\text{NH}_4\text{VF}_4 \cdot 2\text{aq}$, $(\text{NH}_4)_2\text{VF}_5 \cdot \text{aq}$, and $(\text{NH}_4)_3\text{VF}_6$.

Cadmium vanadoxyfluoride $\text{CdVF}_4 \cdot 7\text{aq}$ (Piccini a. Giorgis, *G.* 22 [1] 55).

Cobalt vanadoxyfluoride $\text{CoVF}_4 \cdot 7\text{aq}$.

Nickel vanadoxyfluoride $\text{NiVF}_4 \cdot 7\text{aq}$.

Potassium vanadoxyfluoride $\text{K}_2\text{VF}_6 \cdot \text{aq}$.

Sodium vanadoxyfluoride $\text{Na}_2\text{V}_2\text{F}_{11} \cdot \text{aq}$ = $2\text{VF}_3 \cdot 5\text{NaF} \cdot \text{aq}$ (? $\text{Na}_2\text{VF}_4 \cdot \text{aq}$).

Zinc vanadoxyfluoride $\text{ZnVF}_4 \cdot 7\text{aq}$ (P. a. G., *l.c.*).

Vanadoxyfluorides. (Fluovandates.)

These salts are generally produced by dissolving V_2O_5 in HFAg , adding metallic fluorides, and crystallising; also by dissolving V_2O_5 in solutions of metallic fluorides, and crystallising; some of them are obtained by treating solutions of V_2O_5 in metallic fluoride solutions with reducing agents, and then crystallising. The vanadoxyfluorides have been examined by Baker (*C. J.* 33, 388 [1878]), D'itoe (*C. R.* 105, 1067; 106, 270 [1888]), Piccini a. Giorgis (*G.* 18, 186 [1889]; *G.* 22 [1] 55 [1892]), and Petersen (*B.* 21, 3257 [1888]; more fully in *J. pr.* [2] 40, 193, 271 [1890]). There are still considerable discrepancies between the results obtained by the different observers. For a criticism of Baker's results v. Petersen (*J. pr.* [2] 40, 289-92). The vanadoxyfluorides belong to two main classes: (1) those obtained by dissolving V_2O_5 in HFAg , adding a fluoride (or carbonate), and crystallising; many of these salts are also formed by dissolving V_2O_5 in solutions of fluorides, and crystallising; (2) those obtained by partially reducing solutions of V_2O_5 in HFAg , then adding fluorides, and crystallising. The first class of salts may be divided into (i.) those wherein one atom of O in V_2O_5 is substituted by 2F, and which, therefore, are represented as $x\text{MF}_3 \cdot y\text{VO}_2\text{F}$ (V_2O_5 gives $\text{V}_2\text{O}_4\text{F}_2 = 2\text{VO}_2\text{F}$); and (ii.) those wherein 3O in V_2O_5 is substituted by 6F, and which, therefore, are represented as $x\text{MF}_3 \cdot y\text{VOF}$ (V_2O_5 gives $\text{V}_2\text{O}_3\text{F}_3 = 2\text{VOF}$). Salts of the second class are regarded as compounds of MF^+ with VOF^- , and VOF_2^- is looked on as obtained by substituting 2O in V_2O_5 by 4F (V_2O_5 gives $\text{V}_2\text{O}_3\text{F}_2 = 2\text{VOF}_2$). The salts derived from V_2O_5 , i.e. $x\text{MF}_3 \cdot y\text{VO}_2\text{F}$ and $x\text{MF}_3 \cdot y\text{VOF}$, are often called *fluovandates*, and those derived from V_2O_3 , i.e. $x\text{MF}_3 \cdot y\text{VOF}$, are often called *fluovandates*; the former class of salts will here be called *vanadoxyfluorides*, and the latter *hypervanadoxyfluorides*.

Ammonium vanadoxyfluorides. Three salts are described by Baker (*C. J.* 33, 388 [1878]), and also by Piccini a. Giorgis (*G.* 22 [1] 55, [1892]); the formulæ given by the different experimenters do not agree.

Lamellar ammonium vanadoxyfluoride. This salt was obtained by Baker by dissolving V_2O_5 in NH_4HFAg , and then adding more NH_4HF_2 ; it separates in small yellow, pearly,

hexagonal plates. P. a. G. obtained the salt by dissolving V_2O_5 in a slight excess of $HFAq$, adding NH_4F in the ratio $3NH_4F:2V_2O_5$, and evaporating. B. gives the formula $6NH_4F.V_2O_5.2VOF_2.2aq$; P. a. G. give the formula $3NH_4F.2VOF_2$. If both formulae are expressed as $3NH_4F.2VOF_2$, then $x = 1\frac{1}{2}$ in Baker's formula and -2 in the formula of P. a. G. A salt obtained by Petersen (*J. pr.* [2] 40, 193, 271 [1890]), by a similar process to those used by B. and by P. a. G., was formulated by him as $7NH_4F.4VOF_2.HF$.

Pyramidal ammonium vanadoxyfluoride. Obtained by Baker by adding NH_4HF to a solution of the lamellar salt; P. a. G. prepared the salt by dissolving V_2O_5 in excess of $HFAq$, and exactly neutralising the hot solution by NH_4Aq . This salt crystallises in yellow, simple pyramids (Baker). The formula assigned by B. is $12NH_4F.V_2O_5.2VOF_2$, while that given by P. a. G. is $3NH_4F.VO_2F_2$; Petersen gives the same formula as P. a. G. If Baker's formula is expressed as $3NH_4F.VO_2F_2$, x must be put $= 1\frac{1}{2}$, and $y = 1\frac{1}{2}$.

Acicular ammonium vanadoxyfluoride. Baker obtained this salt by dissolving the pyramidal salt in warm $HFAq$ and allowing to cool; P. a. G. prepared it by a similar reaction. This salt crystallises in pale-yellow acicular prisms; when dry it has the odour of HF ; it acts on glass. The formula given by P. a. G. is $3NH_4F.2VOF_2$; Baker assigned to this salt the formula $3NH_4HF.2VOF_2$, but his analyses were, admittedly, not very trustworthy.

Adopting the formulae given by P. a. G. for the three ammonium vanadoxyfluorides, these salts are represented as

- (1) $3NH_4F.2VOF_2 = (NH_4)_3V_2O_5F_8$,
- (2) $3NH_4F.VO_2F_2 = (NH_4)_3VO_2F_5$,
- (3) $3NH_4F.2VOF_2 = (NH_4)_3V_2O_5F_8$.

A few of the other vanadoxyfluorides seem to belong to one or other of these types; P. a. G. and also Petersen, describe a *potassium vanadoxyfluoride* $8KF.2VOF_2 = K_3V_2O_5F_8$, belonging to the same form as the lamellar ammonium salt. But most of the vanadoxyfluorides described belong to forms which are not represented by the ammonium salts. The following are the principal salts:—

Ammonium salts. $9NH_4F.5VOF_2.3HF$; $7NH_4F.4VOF_2.HF$ (Petersen).

Potassium salts $2KF.VO_2F_2$; $2KF.VOF_2$; $8KF.2VOF_2.HF$; $4KF.VF_3.VOF_2$ (P.).

Sodium salt $3NaF.VOF_2.VO_2F_2$ (P. a. G.).

Zinc salts. $ZnF_2.VO_2F_2.7aq$ (P. a. G.); $ZnF_2.ZnO.2VOF_2.14aq$ (B.).

In none of these compounds does the atomic ratio of V to O exceed 1:2. According to Ditte (*C. R.* 105, 1067; 106, 270 [1889]), many compounds of alkali fluorides with V_2O_5 are formed by heating the constituents together, digesting with water, and crystallising; the atomic ratio of V to O in these compounds, as given by Ditte, is 2:5. The formula assigned to the compounds may be generalised as $xVO_2F_2.yVF_3$; $M = K$ or Na , $x = 1, 3$, and 4, and $y = 1, 2, 4$, and 8. Ditte (*l.c.*) says that crystals of $V_2O_5.4NH_4F.4aq$ are obtained by dissolving V_2O_5 in hot conc. NH_4Aq , and that this compound is formed, along with $V_2O_5.3NH_4F.4aq$, when V_2O_5 is dissolved in cold

conc. NH_4Aq ; but the experiments of Baker, Piccini a. Giorgis, and Petersen, all agree in assigning to the compounds formed in these reactions, formulae wherein the atomic ratio of V to O does not exceed 1:2.

Hypovanadoxyfluorides. (Fluorohypovanadates.) These compounds are formed by partially reducing mixtures of V_2O_5 and fluorides, or carbonates, dissolved in $HFAq$. If sufficient F is assigned to the metal present to form the normal fluoride, then the atomic ratio of V to the remaining F in these compounds is 1:2, and that of V to O is 1:1; the formulae are written $xMF.yVOF_2$. All the salts described by Baker and Piccini a. Giorgis, except one, belong to the form $2MF.VOF_2$ or $M_2F.VOF_2$; these formulae may evidently be written M_2 (or M') VOF_2 .

Ammonium hypovanadoxyfluoride $2NH_4F.VOF_2$, aq ($= (NH_4)_2VOF_2.2aq$) was prepared by Baker (*C. J.* 83, 395) by passing H_2S into a solution of V_2O_5 in $HFAq$, concentrating, filtering, and adding NH_4F . The same salt was prepared by Piccini a. Giorgis (*G. Z.* [1] 55) by electrolytically reducing a solution of NH_4VO_3 in $HFAq$, after adding NH_4F ; also by reducing NH_4VO_3 in $HFAq$ by SO_2Aq , neutralising by NH_4Aq , and adding NH_4F ; and in each case dissolving the crystals that were formed (said by P. a. G. to be $3NH_4F.VOF_2$) in hot $HFAq$, and crystallising. Petersen (*J. pr.* [2] 40, 196) also obtained this salt. The salt crystallises in clear blue monoclinic forms; $a:b = 9.653:1$ (Baker, *l.c.*).

Petersen (*J. pr.* [2] 40, 197) described two other ammonium hypovanadoxyfluorides, $7NH_4F.4VOF_2.5aq$ and $3NH_4F.VOF_2$.

The other hypovanadoxyfluorides described by P. a. G. (*l.c.*) are $2KF.VOF_2$ and $MF.VOF_2.2aq$ where $M = Cd, Co, Ni$ and Zn . The K salt was prepared by reducing V_2O_5 in $HFAq$ by SO_2Aq and adding KF ; the other salts by dissolving MO , or MCO_3 , along with V_2O_5 in $HFAq$, and reducing electrolytically. According to Petersen (*l.c.* pp. 199, 200), the salts $7KF.8VOF_2$ and $8NaF.3VOF_2.2aq$ also exist.

P. a. G. (*l.c.*) remark that the tendency to form highly fluorinated compounds increases in the family V, Nb, Ta as the atomic weight increases; thus, VOF_2 is not affected by a little $HFAq$, while $NbOF_2$ forms $NbOF_3$, and $TaOF_2$ is converted into TaF_5 . They also point out that the three compounds, $ZnF_2.VO_2F_2.7aq$, $ZnF_2.VOF_2.7aq$, and $ZnF_2.VF_3.7aq$, all crystallise with the same number of molecules of water, all contain the same number of atoms, have the same crystalline form, and are geometrically isomorphous.

VANADIUM PENTAFLUORIDE VF_5 . According to Petersen (*J. pr.* [2] 40, 271), this compound exists in a solution of V_2O_5 in conc. $HFAq$. No compound was isolated, nor is any trustworthy evidence given of the existence of VF_5 in solution.

Vanadium, haloid compounds of. When V is heated in excess of Cl the tetrachloride $VOCl_4$ is produced; heating in Br produces the tribromide VBr_3 . V does not combine with I. The haloid compounds of V belong to the forms VX_3 , VX_4 , and VX_5 ; $X = Cl$ in each case, $X = Br$ or F in the one case of VX_3 . The formula VX_4 is molecular; the other formulae are probably molecular. $VOCl_2$, $BiCl_3$, AsI_3 , and PI_3 are the

only dihalides known of members of Group V. Attempts to prepare halides higher than VX_3 have failed. Solutions in water of the haloid compounds of V behave like solutions of the corresponding oxides in haloid acids; VCl_3 Aq like a solution of V_2O_5 in HCl Aq, VX_3 Aq like a solution of V_2O_5 in HXA Aq, and VCl_3 Aq like a solution of V_2O_5 in HCl Aq. VCl_3 is decomposed by heat to VCl_2 and Cl_2 , and heating VCl_3 with H produces VCl_2 . VF_3 combines with metallic fluorides to form *vanadofluorides*, many of which belong to the form M_2VF_6 or M^xVF_6 (v. p. 844). Several oxychlorides and oxybromides of V have been isolated: VOX_2 and VOX_3 , where $X = Cl$ or Br ; also $VOCl$, V_2O_3Cl , and VO_2Cl ; the existence of other oxybromides also is probable. No oxyfluoride has been isolated with certainty. But many compounds exist which may be regarded as containing the oxyfluorides VO_2F , VOF_2 , and VOF_3 , respectively; the compounds $VO_2F \cdot xMF$ and $VOF_2 \cdot xMF$ are obtained by dissolving V_2O_5 and fluorides in HFA and crystallising; they are described as *vanadoxyfluorides* (p. 844); the compounds $VOF_2 \cdot xMF$ are obtained by partially reducing solutions of V_2O_5 and fluorides in HFA Aq, they are described as *hypovanadoxyfluorides* (p. 845).

Vanadium, iodides of. No iodide of V has been isolated. No reaction occurs when vapour of I is passed over VN heated to redness, nor do I and V_2O_5 react at any temperature (Roscoe, *C. J.* [2] 9, 28). I does not react with V_2O_5 when digested therewith for a long time in presence of water or alcohol (Guyard, *Bull.* [2] 25, 351).

Vanadium, nitrides of. V and N combine directly. Two nitrides are known.

VANADIUM MONONITRIDE VN. Mol. wt. not known. Obtained by heating V in a stream of pure N; also by saturating $VOCl_3$ with dry NH_3 , and heating to full whiteness in a stream of NH_3 . Better prepared by heating NH_4VO_3 in the air, and then heating the residue to a full white heat in a stream of dry NH_3 (Roscoe, *C. J.* [2] 8, 844). VN may also be prepared by heating V_2O_5 to whiteness in NH_3 (R., l.c.). VN is a greyish-brown, metal-like powder; heated in air it is oxidised to V_2O_5 , and then to V_2O_6 ; heated with soda-lime it gives off NH_3 .

VANADIUM DINITRIDE VN_2 . A black powder; exposed to air gives off NH_3 and is oxidised. Prepared by saturating $VOCl_3$ with dry NH_3 , heating the solid so obtained in a glass tube as long as NH_3 sublimes, washing the residue with water containing a little NH_3 , and drying *in vacuo* over H_2SO_4 (Roscoe, *C. J.* [2] 6, 349); examined by Uhrlaub, who did not succeed in determining its composition (P. 103, 184; cf. Schafarik, *W. A. B.* 33, 5).

Vanadium, oxides and hydrated oxides of. By gently heating V in air the oxide V_2O_3 is possibly formed, and, on continued heating, oxidation proceeds to V_2O_4 , V_2O_5 , V_2O_6 , and finally V_2O_7 . The oxides V_2O_4 , V_2O_5 , and V_2O_6 are also formed by reducing V_2O_5 by heating with H or K. Several oxides intermediate between V_2O_4 and V_2O_5 seem also to exist. The oxides V_2O_4 , V_2O_5 , V_2O_6 , and V_2O_7 are feebly basic; V_2O_4 and V_2O_5 are also 'acidic'. The oxides of V correspond in composition with the oxides of N; corresponding oxides of Bi

are known. The names generally given to the oxides of V do not, unfortunately, tally with the names given to the corresponding oxides of N; thus, V_2O_3 is generally called hypovanadous oxide, while NO is called nitric oxide; V_2O_5 is called vanadic oxide, while the name nitrogen peroxide is often quite wrongly applied to NO_2 . The mol. w. of none of the oxides of V is known.

? VANADIUM MONOXIDE (? V_2O). When the powdered metal is slowly heated in a current of air it glows brightly, with absorption of oxygen, forming in the first place a brown oxide (V_2O or V_2O_2); and on further heating this oxide again glows, and passes through the black trioxide and blue tetroxide to pentoxide (Roscoe, *C. J.* [2] 8, 357). This statement seems to contain all that is known of an oxide lower than V_2O_3 .

VANADIUM DIOXIDE V_2O_4 . (*Hypovanadous oxide*.) This substance was supposed by Berzelius (P. 22, 1) to be V; Roscoe (T. 1868, 1) proved it to be an oxide with the atomic ratio $V:O = 1:1$. The mol. w. is not known; the formula is generally written V_2O_4 rather than VO , as the double formula is, on the whole, more in keeping with the reactions of the compound.

Formation.—1. By heating one of the higher oxides with K (Berzelius, l.c.).—2. By passing vapour of $VOCl_3$, mixed with much dry H, over red-hot charcoal (Schafarik, A. 109, 85).—3. By strongly heating V_2O_5 and V_2O_6 , mixed in the ratio $V_2O_5:V_2O_6$, out of contact with air (Petersen, *J. pr.* [2] 40, 193).

Preparation.—A mixture of much dry H and vapour of $VOCl_3$ (q. v. p. 854) is passed through a hard glass tube containing powdered charcoal and kept red hot. Some solid oxychlorides are deposited on the cooler parts of the tube, while the V_2O_4 remains mixed with the C. The contents of the tube are then strongly heated in a current of dry H to remove traces of Cl compounds; and the grey metal-like V_2O_4 is separated from the C (Roscoe, *C. J.* [2] 6, 334). When Zn, Cd, or Na-amalgam is added to a solution of V_2O_4 in H_2SO_4 Aq (prepared by dissolving the oxide in hot conc. acid and diluting with 50 pts. water), the liquid becomes blue, green, and finally lavender. The lavender solution absorbs O very rapidly; exposure to the air for a few seconds causes the colour to change to deep chocolate-brown. By determining the quantity of standardised $KMnO_4$ Aq decolourised by the lavender solution, Roscoe (*C. J.* [2] 6, 334) proved that this solution contained V_2O_4 , probably combined with SO_2 . After passing air into the lavender solution until it becomes permanently blue, the solution contains V_2O_5 ; if the free acid in the lavender solution is neutralised by zinc, and the liquid is then exposed to the air until permanently brown, and a little acid is then added, a green solution is formed which contains V_2O_6 (R., l.c.).

Properties and Reactions.—A light-grey, lustrous powder; or a lustrous, metal-like, crystalline crust, S.G. 8.64; very brittle; fuses at a very high temperature. Heated to redness in air, V_2O_4 burns to V_2O_5 ; heated in O, burns to V_2O_6 . Insoluble in water; dissolves in dilute acids, giving a lavender solution, which bleaches strongly; from these solutions KOHAq or

NH_4Aq ppm. a brown hydrated oxide, which rapidly oxidises (Brierley, *C. J.* 49, 824). According to Petersen (*J. pr.* [2] 40, 194), V_2O_5 dissolves in HFAq , and on evaporation, solution of the residue in water, and evaporation over H_2SO_4 , blue, microscopic crystals are obtained, which are, perhaps, $\text{VOF}_3 \cdot 2\text{aq}$; no analyses were made. Addition of alkali fluorides to V_2O_5 in HFAq produces various compounds of the form $x\text{VOF}_3 \cdot y\text{MF}$ (v. HYPOVANADOXYFLUORIDES, p. 846).

HYDRATE OF VANADIUM DIOXIDE. By adding NH_4Aq to a lavender-coloured solution of V_2O_5 in $\text{H}_2\text{SO}_4\text{Aq}$, Brierley (*C. J.* 49, 824) obtained a deep-purple gelatinous pp. which he said was hydrated V_2O_5 ; the pp. rapidly oxidised in the air.

VANADIUM TRIOXIDE V_2O_5 . (*Vanadous oxide Vanadium sesquioxide*.) Mol. w. not known. This compound was represented by Berzelius as VO ($\text{V} = 68.5$, $\text{O} = 8$).

Formation.—1. By heating V_2O_5 to redness in H (Schafarik, *A.* 109, 85). The presence of traces of P_2O_5 prevents reduction (Roscoe, *C. J.* [2] 6, 331).—2. By heating V_2O_5 in a carbon crucible (Berzelius, *P.* 22, 1).

Preparation.—Pure V_2O_5 is heated in perfectly pure and dry H until the substance ceases to lose weight; the tube is allowed to cool completely in H , and then a stream of dry air is passed through it (Roscoe, *C. J.* [2] 6, 331). When a solution of V_2O_5 in conc. H_2SO_4 is much diluted, and then treated with Mg until the liquid is green, this solution contains V_2O_5 , combined with SO_2 (v. VANADOUS SALTS, *infra*). A similar solution is obtained from the lavender solution of V_2O_5 in $\text{H}_2\text{SO}_4\text{Aq}$ (prepared from V_2O_5 in H_2SO_4 , v. *supra*) by neutralising free acid by zinc, exposing to the air, and adding a little acid (Roscoe, *C. J.* [2] 6, 337).

Properties and Reactions.— V_2O_5 is a black powder, resembling graphite; or, formed by reducing VOCl_3 by H , it is a black, lustrous, crystalline crust. S.G. 4.72 at 16° . Does not fuse in the blowpipe flame. When warm V_2O_5 is exposed to the air it glows and oxidises to V_2O_5 ; and even at the ordinary temperature it takes up O , being changed after some months to V_2O_5 (R., c.). Heated in Cl gives V_2O_5 and VOCl_3 (R., l.c.). Heated in NO_2 to 300° – 400° V_2O_5 is oxidised to V_2O_5 (Sabatier & Senderens, *C. R.* 115, 236). Heating to redness in H_2S produces V_2S_5 (Kay, *I. J.* 87, 728). V_2O_5 dissolves in hot conc. LSO_4 , forming $\text{V}_2\text{O}_5 \cdot x\text{SO}_3$ (v. VANADOUS SALTS, *infra*). V_2O_5 dissolves in HFAq , and $\text{VF}_3 \cdot \text{H}_2\text{O}$ has been isolated from this solution (v. VANADIC FLUORIDE, p. 844).

HYDRATE OF VANADIUM TRIOXIDE. By adding COH_4Aq , or NH_4Aq , to an aqueous solution of $\text{V}_2\text{O}_5 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ (v. *infra*) Brierley (*C. J.* 49, 824) obtained a dirty green, gelatinous pp., which oxidised rapidly in air. According to B., this pp. was hydrated V_2O_5 .

VANADOUS SALTS $\text{V}_2\text{O}_5 \cdot x\text{X}$ ($\text{X} = \text{acidic oxide}$ or $\text{V}_2\text{B}_2\text{O}_7$ ($\text{B} = \text{acidic radicle}$)). Only one salt derived from an oxyacid has been certainly isolated; it has the composition $\text{V}_2\text{O}_5 \cdot 4\text{SO}_3 \cdot x\text{H}_2\text{O}$, the formula may be written $\text{V}_2\text{H}_2(\text{SO}_4)_x \cdot y\text{H}_2\text{O}$.

Vanadous tetrasulphate, or acid vanadous sulphate, $\text{V}_2\text{O}_5 \cdot 4\text{SO}_3 \cdot x\text{H}_2\text{O}$ or $\text{V}_2\text{H}_2(\text{SO}_4)_x \cdot y\text{H}_2\text{O}$.

A hydrate with $x=3$ or $y=2$ was obtained

by Gerland (*B.* 10, 2111 [1877]) by heating a solution of V_2O_5 in a large excess of conc. H_2SO_4 for a long time at 120° , and treating the blue crystalline crusts thus formed (consisting chiefly of $\text{V}_2\text{O}_5 \cdot 3\text{SO}_3 \cdot 2\text{aq}$, v. HYPOVANADIC SALTS, p. 848) with boiling water, when $\text{V}_2\text{O}_5 \cdot 4\text{SO}_3 \cdot 8\text{H}_2\text{O}$ remained. G. supposed that reduction of V_2O_5 was effected by dust in the air.

Brierley (*C. J.* 49, 822 [1886]) prepared $\text{V}_2\text{O}_5 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ ($= \text{V}_2\text{H}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$) by electrolysis a solution of V_2O_5 in H_2SO_4 . The solution was prepared by reducing V_2O_5 in conc. H_2SO_4 , after dilution, by SO_2 . The deep-blue solution was placed in a Pt dish which formed the negative electrode, and a porous pot containing dilute $\text{H}_2\text{SO}_4\text{Aq}$ was arranged so that it just touched the surface of the liquid in the Pt dish; a plate of Pt immersed in the $\text{H}_2\text{SO}_4\text{Aq}$ formed the positive electrode. The Pt dish was warmed during the process, so that electrolysis and evaporation proceeded together. Electrolysis was continued until the liquid was deep green, and a drop placed in a little water showed no trace of blue colour. Conc. H_2SO_4 , equal to twice the bulk of the green liquid, was added; after 24 hours the green, sandy pp. was collected, washed with conc. alcohol, and dried over H_2SO_4 in coal-gas. The salt dissolved in water, and alkali ppd. from this solution a dirty-green gelatinous substance, said by B. to be $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$. This pp. dissolved in an aqueous solution of $\text{V}_2\text{O}_5 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$, forming a chocolate-brown solution, giving a lustrous green solid on evaporation, which dissolved in water to form a brown solution. B. concluded that the brown solution contained a compound of V_2O_5 and SO_2 , more basic than $\text{V}_2\text{O}_5 \cdot 4\text{SO}_3$.

Gerland (*B.* 11, 106 [1878]) mentions the normal vanadous sulphate $\text{V}_2(\text{SO}_4)_3$ ($= \text{V}_2\text{O}_5 \cdot 3\text{SO}_3$) as if he had prepared it; no details are given.

VANADIUM TRIOXIDE V_2O_5 . (*Hyponanadite oxide*.) Mol. w. not known. Represented by Berzelius as VO_2 ($\text{V} = 68.5$, $\text{O} = 8$).

Formation.—1. By allowing V_2O_5 to absorb O from the air (cf. HYPOVANADO-VANADIC OXIDES, p. 851).—2. By strongly heating a mixture of 5 pts. V_2O_5 and 6 pts. V_2O_5 in absence of air.—3. By the electrolysis of molten V_2O_5 (Buff & Wöhler, *A.* 110, 277).—4. By heating $\text{V}_2\text{O}_5 \cdot \text{Cl}_3$ in a stream of CO_2 (Crow, *C. J.* [2] 15, 453).

Preparation.—A solution of V_2O_5 in H_2SO_4 , obtained by reducing V_2O_5 in conc. H_2SO_4 by SO_2 , is ppd. by $\text{Na}_2\text{CO}_3\text{Aq}$, and the pp. is washed and dried by heating *in vacuo* (Berzelius, *P.* 22, 1).—2. V_2O_5 is exposed to the air for some months, until the colour has changed to blue (Roscoe, *J. J.* [2] 6, 338).—3. V_2O_5 is dissolved in hot conc. HClAq ; when Cl ceases to be given off the liquid is saturated with H_2S , filtered from S , evaporated to dryness at 100° and the $\text{V}_2\text{O}_5 \cdot \text{Cl}_3$ thus formed is heated to redness in a stream of dry CO_2 (Crow, *l.c.* pp. 457, 458).

Properties and Reactions.—A blue, lustrous, crystalline powder; prepared by heating $\text{V}_2\text{O}_5 \cdot \text{Cl}_3$ in CO , it forms a dark-green, amorphous powder (Crow, *l.c.*). Infusible at a high temperature. Insoluble in water. When kept in a loosely-stoppered bottle V_2O_5 gradually absorbs O , forming V_2O_5 (Crow, *l.c.*). Dissolves easily in acids, forming bright-blue liquids; the same solutions are obtained by the action of moderate

reducers, such as SO_2Aq , H_2SAq , or $\text{H}_2\text{C}_2\text{O}_4\text{Aq}$, on solutions of V_2O_5 in acids, also by passing air into V_2O_5 in $\text{H}_2\text{SO}_4\text{Aq}$ until the liquid becomes permanently blue (Roscoe, *l.c.*; *v. infra*, HYPOVANADIC SALTS). Petersen (*J. pr.* [2] 40, 194) supposed that the blue microscopic crystals he obtained, by dissolving V_2O_5 in excess of HFAq and evaporating were $\text{VOF}_2\cdot x\text{aq}$, but he did not obtain enough to make an analysis. V_2O_5 dissolves readily in alkali solutions, forming hypovanadates, $\text{M}_2\text{V}_2\text{O}_8$ (*q. v.* under VANADIUM OXIDES, AND SALTS AND DERIVATIVES THEREOF, p. 853).

HYDRATES OF HYPOVANADIC OXIDE. By adding $\text{Na}_2\text{CO}_3\text{Aq}$, drop by drop, to a solution of V_2O_5 in HClAq or $\text{H}_2\text{SO}_4\text{Aq}$, till the supernatant liquid was colourless, filtering rapidly in CO_2 , and drying on a porous tile over H_2SO_4 *in vacuo*, Crow (*l.c.*) obtained the black, amorphous *heptahydrate* $\text{V}_2\text{O}_5\cdot 7\text{aq}$; and on heating this in CO_2 for some hours at 100° he obtained the *trihydrate* $\text{V}_2\text{O}_5\cdot 3\text{aq}$.

HYPOVANADIC (or vanadyl) SALTS $\text{V}_2\text{O}_5\cdot x\text{X}$ (X=acidic oxide). Only a few compounds of V_2O_5 with acidic oxides have been isolated. The sulphates have been studied more than any other salts; they are most simply represented as $\text{V}_2\text{O}_5\cdot x\text{SO}_3\cdot y\text{H}_2\text{O}$. The compound $\text{V}_2\text{O}_5\cdot 2\text{SO}_3$ may be called the normal sulphate; the formula may be expressed as $\text{V}_2\text{O}_5(\text{SO}_3)_2$ or $\text{VO}\cdot\text{SO}_3$. The compound $\text{V}_2\text{O}_5\cdot 3\text{SO}_3\cdot 6\text{H}_2\text{O}$ may be called acid sulphate; the formula may be expressed as $\text{V}_2\text{O}_5\cdot \text{SO}_3(\text{SO}_3\text{H})_2\cdot 5\text{H}_2\text{O}$ or $(\text{VO})_2\text{H}_2(\text{SO}_3)_2\cdot 5\text{H}_2\text{O}$, or $(\text{VO}\cdot\text{SO}_3)_2\cdot \text{H}_2\text{SO}_4\cdot 5\text{H}_2\text{O}$; or it may be written $\text{V}_2\text{O}_5\cdot 2\text{SO}_3\cdot \text{H}_2\text{SO}_4\cdot 5\text{H}_2\text{O}$. When the formulae of the compounds of V_2O_5 with acidic oxides are written $\text{V}_2\text{O}_5\cdot \text{X}$ the compounds are generally called *hypovanadic salts*; when the formulae are written $\text{V}_2\text{O}_5\cdot x\text{R}$ (R=acidic radicle) the name *divanadyl salts* is usually given to the compounds; and when these compounds are regarded as $\text{VO}\cdot x\text{R}$, it is customary to call them *vanadyl salts*. Hypovanadic sulphates are obtained (1) by dissolv-

H_2SO_4 and heating to the boiling-point of the liquid for a long time. The salt separated as a green-blue powder; insoluble in water, gold or hot; insoluble HClAq and H_2SO_4 . (G. does not say how the salt was obtained pure for analysis; no analyses are given of the salt prepared exactly as described above.) Various *hydrates* are described by G. obtained by different processes. Crow (*C. J.* [2] 15, 456 [1876]), obtained the *heptahydrate* by repeatedly treating hexahydrated trisulphate (*v. infra*) with absolute alcohol.

Hypovanadic trisulphate, or acid divanadyl sulphate, $\text{V}_2\text{O}_5\cdot 3\text{SO}_3\cdot x\text{H}_2\text{O}$ or $(\text{VO})_2\text{H}_2(\text{SO}_3)_3\cdot y\text{H}_2\text{O}$ [$y=x-1$]. (*Acid vanadyl sulphate* $(\text{VO}\cdot\text{SO}_3)_2\cdot \text{H}_2\text{SO}_3\cdot y\text{H}_2\text{O}$.) Hydrates with $x=4$ and 3 (or $y=3$ and 2) were prepared by Gerland (*B. 10*, 2, 109); and a hydrate with $x=6$ (or $y=5$) by Crow (*C. J.* [2] 15, 455).

By dissolving V_2O_5 in a large excess of conc. H_2SO_4 , heating for a long time at c. 120° , and drying the small, blue, transparent crystals that formed on a porous tile over H_2SO_4 , Gerland obtained a substance which gave analytical results approaching those required by the formula $\text{V}_2\text{O}_5\cdot 3\text{SO}_3\cdot 4\text{H}_2\text{O}$. The salt was not obtained quite free from admixed $\text{V}_2\text{O}_5\cdot 4\text{SO}_3\cdot x\text{H}_2\text{O}$. This *tetrahylate* was partially decomposed by cold water, giving lustrous scales which, after washing with alcohol and ether and drying over H_2SO_4 , had the composition of a *trihydrate*, $\text{V}_2\text{O}_5\cdot 3\text{SO}_3\cdot 3\text{H}_2\text{O}$.

Crow obtained a *hexahydrate* $\text{V}_2\text{O}_5\cdot 3\text{SO}_3\cdot 6\text{H}_2\text{O}$, by reducing by SO_2 a solution of V_2O_5 in conc. H_2SO_4 , heating at 100° for some time, drying the light-blue crystals that separated on a tile, removing acid by washing with ether, and drying by pressure between paper. The crystals deliquesced in air to a blue syrup; they were insoluble in ether, and scarcely soluble in absolute alcohol.

The formulae of the various hydrated hypovanadic sulphates are as follows:—

<i>Hypovanadic sulphates</i> ;	or	<i>Divanadyl sulphates</i> ;	or	<i>Vanadyl sulphates</i> .
$\text{V}_2\text{O}_5\cdot 2\text{SO}_3$		$\text{V}_2\text{O}_5(\text{SO}_3)_2$		$\text{VO}\cdot\text{SO}_3$ (Gerland).
$\text{V}_2\text{O}_5\cdot 2\text{SO}_3\cdot 3\text{H}_2\text{O}$		$\text{V}_2\text{O}_5(\text{SO}_3)_2\cdot 3\text{H}_2\text{O}$		$2(\text{VO}\cdot\text{SO}_3)\cdot 3\text{H}_2\text{O}$ (G.)
$\text{V}_2\text{O}_5\cdot 2\text{SO}_3\cdot 4\text{H}_2\text{O}$		$\text{V}_2\text{O}_5(\text{SO}_3)_2\cdot 4\text{H}_2\text{O}$		$\text{VO}\cdot\text{SO}_3\cdot 2\text{H}_2\text{O}$ (Crow, confirming Berzelius).
$\text{V}_2\text{O}_5\cdot 2\text{SO}_3\cdot 7\text{H}_2\text{O}$		$\text{V}_2\text{O}_5(\text{SO}_3)_2\cdot 7\text{H}_2\text{O}$		$2(\text{VO}\cdot\text{SO}_3)\cdot 7\text{H}_2\text{O}$ (G., also C.)
$\text{V}_2\text{O}_5\cdot 2\text{SO}_3\cdot 10\text{H}_2\text{O}$		$\text{V}_2\text{O}_5(\text{SO}_3)_2\cdot 10\text{H}_2\text{O}$		$\text{VO}\cdot\text{SO}_3\cdot 5\text{H}_2\text{O}$ (G.)
$\text{V}_2\text{O}_5\cdot 2\text{SO}_3\cdot 13\text{H}_2\text{O}$		$\text{V}_2\text{O}_5(\text{SO}_3)_2\cdot 13\text{H}_2\text{O}$		$2(\text{VO}\cdot\text{SO}_3)\cdot 13\text{H}_2\text{O}$ (G.)
$\text{V}_2\text{O}_5\cdot 3\text{SO}_3\cdot 3\text{H}_2\text{O}$		$(\text{VO})_2\text{H}_2(\text{SO}_3)_3\cdot 2\text{H}_2\text{O}$		$2(\text{VO}\cdot\text{SO}_3)\cdot \text{H}_2\text{SO}_3\cdot 2\text{H}_2\text{O}$ (G.)
$\text{V}_2\text{O}_5\cdot 3\text{SO}_3\cdot 4\text{H}_2\text{O}$		$(\text{VO})_2\text{H}_2(\text{SO}_3)_3\cdot 3\text{H}_2\text{O}$		$2(\text{VO}\cdot\text{SO}_3)\cdot \text{H}_2\text{SO}_3\cdot 3\text{H}_2\text{O}$ (G.)
$\text{V}_2\text{O}_5\cdot 3\text{SO}_3\cdot 5\text{H}_2\text{O}$		$(\text{VO})_2\text{H}_2(\text{SO}_3)_3\cdot 5\text{H}_2\text{O}$		$2(\text{VO}\cdot\text{SO}_3)\cdot \text{H}_2\text{SO}_3\cdot 5\text{H}_2\text{O}$ (C.)

ing V_2O_5 in hot conc. H_2SO_4 and boiling; (2) by dissolving V_2O_5 in conc. H_2SO_4 , reducing by SO_2 , or $\text{H}_2\text{C}_2\text{O}_4$, and evaporating; (3) by dissolving V_2O_5 in conc. H_2SO_4 and boiling in the air for some time. In reaction (5) $\text{V}_2\text{O}_5\cdot x\text{SO}_3$ seems to be formed and then partially reduced, by dust or products of combustion of coal-gas, to $\text{V}_2\text{O}_5\cdot x\text{SO}_3$; the products are mixtures of $\text{V}_2\text{O}_5\cdot x\text{SO}_3$ and $\text{V}_2\text{O}_5\cdot x\text{SO}_3$ (Gerland, *B. 11*, 98).

Hypovanadic disulphate, or normal divanadyl sulphate, $\text{V}_2\text{O}_5\cdot 2\text{SO}_3$, or $\text{V}_2\text{O}_5(\text{SO}_3)_2$. (*Vanadyl sulphate* $\text{VO}\cdot\text{SO}_3$.) Prepared by Gerland (*B. 10*, 2109 [1877]; supplementing *B. 9*, 869) by dissolving V_2O_5 in a large excess of conc.

Bevan (*C. N.* 38, 294) obtained *divanadyl dithionate* by adding $\text{BaS}_2\text{O}_8\text{Aq}$ to $\text{V}_2\text{O}_5(\text{SO}_3)_2\text{Aq}$, filtering, and evaporating *in vacuo*; the salt was not obtained pure. By dissolving V_2O_5 in KNO_3Aq Berzelius (*P. 22*, 1) obtained a blue liquid which probably contained *hypovanadic nitrate*; but no solid could be isolated, as on evaporation to dryness decomposition occurred, with formation of V_2O_5 . V_2O_5 also dissolves in $\text{H}_3\text{PO}_4\text{Aq}$; on evaporation at 50° blue crystals are obtained, which deliquesce to a blue syrup; these crystals are probably *hypovanadic phosphate*, but no analyses are given (*B. l.c.*). Berzelius obtained what were probably com-

pounds of V_2O_5 with As_2O_3 , B_2O_3 , CrO_3 , MoO_3 , and a few other acidic oxides (*Lehrbuch* [5th ed.] 3, 1053).

VANADIUM PENTOXIDE V_2O_5 . (*Vanadic oxide. Vanadic anhydride.*) Mol. w. not known. Represented by Berzelius as VO_2 ($V = 68.5$, $O = 8$).

Formation.—1. By strongly heating any of the lower oxides in air or O_2 .—2. By heating NH_4VO_3 in air to dull redness.—3. By decomposing $VOCl_3$ by water.—4. By heating $V_2O_3 \cdot 4SO_3$ 9aq to bright redness (Brierley, *C. J.* 49, 824).

Preparation.—Pure $VOCl_3$ is decomposed by water, and the *ppd.* V_2O_5 is washed till the washings are free from acid ($HClAq$ is produced) and heated until dry (Schafarik, *J. pr.* 76, 142). For the preparation of V_2O_5 from *vanadinite* and other sources of *V* compounds, *v. VANADIUM, Preparation of* (p. 841).

Properties.—A pale-yellow powder, with a reddish tinge. When heated to full redness out of contact with any reducing agents, V_2O_5 melts, and solidifies on cooling to a mass of yellow-red, crystalline needles, appearing ruby-red by transmitted light; should the V_2O_5 used contain V_2O_3 , which is often the case when the V_2O_5 is prepared by heating NH_4VO_3 , the solid obtained by fusion and cooling appears violet to nearly black, and does not seem to be crystalline (Berzelius, *P.* 22, 1). As molten V_2O_5 cools nearly to its solidifying-point much heat is given out, and the mass glows until solidification is complete (*ib.*, *l.c.*). V_2O_5 is said not to be changed at a white heat, provided no trace of a reducing agent is present (*ib.*, *l.c.*); but according to Read (*C. J.* 65, 313 [1894]) molten V_2O_5 gives off O , producing V_2O_3 , which on cooling in air takes up O , forming steel-blue crystals of V_2O_3 . The crystals of V_2O_5 are rhombic (*v. Nordenskjöld*, *P.* 112, 160). S.G. (crystalline) 3.5 at 20° (Schafarik, *J. pr.* 76, 142). V_2O_5 is odourless and tasteless; it reddens moist litmus paper; 1,000 pts. boiling water dissolve scarcely 1 pt. V_2O_5 (*ib.*, *l.c.*). With molten alkalis or alkali carbonates V_2O_5 produces *vanadates* (*q.v.* p. 851). V_2O_5 dissolves in conc. H_2SO_4 , $HClAq$, HNO_3Aq , or $HFAq$ (*cf. VANADIC SALTS*, p. 850).

According to Ditté (*C. R.* 101, 698), V_2O_5 exists in three forms: (1) *red*, obtained by heating NH_4VO_3 in a closed crucible, treating with HNO_3 , and repeatedly heating to redness; (2) *yellow*, obtained by heating NH_4VO_3 to 440° in a stream of air; and (3) *crystalline*, obtained by treating the yellow form with HNO_3 , and then fusing. D. says that the red form is somewhat soluble in water, 1,000 c.c. dissolving 8 g. at 20° ; that the yellow form is very slightly soluble, and the crystalline form is insoluble, in water. He also says that the red form absorbs water from the air, producing hydrates with $2H_2O$ and $5H_2O$; and that addition of $NHCl$, KCl (and other salts) to an aqueous solution of the red variety causes *ppn.* of a hydrate of the yellow form of V_2O_5 , which hydrate, when dry, is a dark-red powder having the composition $V_2O_5 \cdot 2H_2O$ ($= H_2V_2O_7$) and is almost insoluble in water. (No analyses are given by D.)

Reactions.—1. When heated and kept molten, V_2O_5 is formed, and this absorbs O as it cools in air and forms V_2O_3 (Read, *C. J.* 65, 313 [1894]). 2. Heated to redness in hydrogen till it ceases to lose weight, V_2O_5 is reduced to V_2O_3 (Schafarik,

A. 109, 85); traces of P_2O_5 prevent the reduction (Roscoe, *C. J.* [2] 6, 831).—3. Heating with potassium produces V_2O_3 (Berzelius, *P.* 22, 1).—4. V_2O_5 is produced by heating V_2O_3 in a carbon crucible (*ib.*, *l.c.*). For action of Mg , Zn , &c. on solutions of V_2O_5 , *v. VANADIC SALTS*, (p. 850).—5. When mixed with carbon and heated in chlorine, V_2O_5 yields $VOCl_3$ (Roscoe, *C. J.* [2] 6, 342).—6. Electrolysis of molten V_2O_5 produces V_2O_3 (Bull. a. Wöhler, *A.* 110, 277).—7. According to Ditté (*C. R.* 103, 55), fusion with potassium cyanide produces V_2O_3 (N , K_2O , and CO , being also formed). Carnot (*S. R.* 184, 1803, 1850; 105, 119) says that a boiling solution of potassium cyanide produces KVO_3 (CO_2 and N being given off); and that by dropping V_2O_5 into excess of boiling $KCNaq$ there is formed $K_2V_2O_7$ (with evolution of N and CO_2). No analyses are given either by D. or C.—8. Ditté (*C. R.* 103, 55) asserts that the products of the interaction of V_2O_5 and potassium iodide or bromide are $K_2V_2O_7$, KVO_3 , and I or Br . The reactions are said to occur between V_2O_5 and molten KI or KBr ; and $KIAq$ is said to react in the same way as the molten salt.—9. When V_2O_5 is heated with molten boron trioxide, a pale-yellow glass is formed, which is said by Guyard (*Bl.* [2] 40, 351) to be a vanadic borate; no analyses, composition, or methods of purification are given.—10. V_2O_5 dissolves in hot conc. sulphuric acid, forming $V_2O_5 \cdot xSO_3$, generally along with more or less $V_2O_3 \cdot xSO_3$ (*v. VANADIC SALTS*, p. 850).—11. V_2O_5 dissolves in conc. hydrochloric acid; Cl is given off on heating; after the passage of H_2S followed by evaporation at 100° the oxychloride $VO_2Cl_2 \cdot 2aq$ is obtained (Crown, *C. J.* 30, 457; *cf. VANADIUM DIOXYMONOCHLORIDE*, p. 854).—12. By dissolving V_2O_5 in conc. hydrochloric acid in presence of platinum chloride, Brauner (*M.* 3, 58) obtained large tablets having the composition $2(VOCl_2 \cdot PtCl_4) \cdot 21aq$.—13. An oxyiodide $2VOI_2 \cdot 9aq$ is obtained, according to Ditté (*C. R.* 102, 1310), by adding excess of hydriodic acid to a warm aqueous solution of red V_2O_5 , removing free I by shaking with silver powder, filtering, and evaporating *in vacuo*. (No analyses are given).—14. V_2O_5 dissolves in hydrofluoric acid, forming a pale-yellow solution, the colour of which becomes deeper on dilution (Piccini a. Giorgis, *G.* 22 [1] 55). Petersen (*J. pr.* [2] 40, 271) supposed that a solution in conc. $HFAq$ contained VF_3 ; but he did not separate this compound, nor does he give any direct evidence in favour of its existence beyond the preparation from the solution of V_2O_5 in $HFAq$ of a compound which may be represented as $xMF \cdot VF_3 \cdot yVOF$, and other compounds of the forms $xMF \cdot yVOF$, and $xMF \cdot yVO_2F$. By adding metallic fluorides to solutions of V_2O_5 in $HFAq$, and crystallising, vanadoxyfluorides are formed; these compounds are of the forms $xMF \cdot yVOF$, and $xMF \cdot yVO_2F$ (*v. VANADOXYFLUORIDES*, p. 844).—15. Vanadoxyfluorides are also formed by dissolving V_2O_5 in alkali fluoride solutions, and crystallising (*cf. infra, Combinations*, No. 5).—16. If a solution of V_2O_5 in hydrofluoric acid is partially reduced, and then evaporated with metallic fluorides, hypovanadoxyfluorides (*q.v.* p. 845) are formed; these salts are of the form $xMF \cdot yVOF$.—17. By boiling V_2O_5 with hydrogen peroxide solution, a

black liquid was obtained that deposited a black-brown crust of indefinite composition (Cammerer, *Chem. Zeit.* 19, 957).—18. By fusion with alkali or alkali carbonates vanadates are formed (v. VANADATES, p. 851).

Combinations.—1. With *wolff*, but not directly, to form $V_2O_5 \cdot H_2O$ and $V_2O_5 \cdot 2H_2O$ (v. *Metavanadic acid* and *Pyrovanadic acid*, under VANADIUM OXYACIDS, AND SALTS AND DERIVATIVES THEREOF, p. 851).—2. With various *acidic oxides*: (1) With SO_2 to form $V_2O_5 \cdot xSO_2$, formed by dissolving V_2O_5 in hot conc. H_2SO_4 ; (2) with As_2O_3 to form $V_2O_5 \cdot xAs_2O_3$; (3) with P_2O_5 to form $V_2O_5 \cdot xP_2O_5$; (4) with IO_2 to form $V_2O_5 \cdot xIO_2$; (5) with MoO_3 to form $V_2O_5 \cdot xMoO_3$; (6) with WO_3 to form $V_2O_5 \cdot xWO_3$; (7) with P_2O_5 and SiO_2 to form $V_2O_5 \cdot xP_2O_5 \cdot ySiO_2$. Most of these compounds combine with the stronger bases M_2O and MO to form salt-like compounds. The compounds of V_2O_5 with SO_2 are described as *vanadic sulphates* under VANADIC SALTS (*infra*); the compounds with other acidic oxides are described respectively as *arseno-vanadic acids and salts*, *iodo-vanadic acids*, *thiobido-vanadic acids and salts*, *phospho-vanadic acids and salts*, *phospho-silico-vanadic acid*, and *tungsto-vanadic acids and salts*, under VANADIUM OXYACIDS, AND SALTS AND DERIVATIVES THEREOF (v. pp. 853-4).—3. With *vanadium tetroxide* to form oxides intermediate between V_2O_5 and V_2O_4 (v. HYPOVANADO-VANADIC OXIDES, p. 851).—4. With *vanadium trioxide* to form V_2O_4 ; produced by heating equivalent weights of the two oxides out of contact with air (Berzelius, *P.* 22, 1; Petersen, *J. pr.* [2] 40, 193).—5. With *alkali fluorides*. According to Ditte (*C. R.* 105, 1067; 106, 270), several compounds of the form $xV_2O_5 \cdot yMF$ are formed by fusing V_2O_5 with alkali fluorides, extracting with water, and crystallising; D. gives formulae where $x=1, 3$ and 4, $y=1, 2, 4$ and 8, and $M=K$ and Na ; but he does not give analyses of the salts (v. VANADOXYFLUORIDES, p. 844).

HYDRATES OF VANADIC OXIDE. The hydrates $V_2O_5 \cdot H_2O = HVO_3$ and $V_2O_5 \cdot 2H_2O = H_2V_2O_6$ have been isolated; these compounds are acids (v. VANADIC ACIDS, p. 851). Ditte (*C. R.* 101, 698) asserts, without giving analyses, that a pentahydrate $V_2O_5 \cdot 5H_2O$ is formed by absorption of water from the air by the red form of V_2O_5 (v. VANADIUM PENTOXIDE, *Properties*, p. 849).

VANADIC SALTS $V_2O_5 \cdot xX$ (X =acidic oxide). A few compounds of this form have been isolated. The sulphates have been better studied than the other salts. Two sulphates, $V_2O_5 \cdot 2SO_3 \cdot xH_2O$ and $V_2O_5 \cdot 8SO_3 \cdot xH_2O$, have been isolated. If x is taken to be 2 in the first salt and 8 in the second, then the formulae may be written as $(VO_2)_2SO_4 \cdot H_2SO_4 \cdot H_2O$ and $(VO_2)_2SO_4 \cdot 2H_2SO_4 \cdot H_2O$ respectively. $[(VO_2)_2SO_4 \cdot H_2SO_4 \cdot H_2O = V_2O_5 \cdot 2SO_3 \cdot 2H_2O]$; $[(VO_2)_2SO_4 \cdot 2H_2SO_4 \cdot H_2O = V_2O_5 \cdot 8SO_3 \cdot 3H_2O]$. If the salts are anhydrous, as seems most probable from the analyses, then the formulae may be written $(VO_2)_2SO_4 \cdot SO_3$ and $(VO_2)_2SO_4 \cdot 2SO_3$, respectively. Neither of the salts can be regarded as the normal salt. The sulphates are obtained by dissolving V_2O_5 in hot conc. H_2SO_4 .

Vanadic disulphate $V_2O_5 \cdot 2SO_3$ (? xH_2O). Prepared by Berzelius (*P.* 22, 39); examined also by Fritzsche (*J. pr.* 53, 93), Gerland (*B.* 11,

98), and Münzig (*C. C.* 1899 (ii.) 908). The salt seems to be without water of crystallisation; F. (*l.c.*) says it crystallises with H_2O . V_2O_5 is dissolved in hot conc. H_2SO_4 , and the solution is boiled for a considerable time, when small crystals separate, some of which are brown and some ruby-red, lustrous, and transparent. The crystals are heated in a bath of molten lead until SO_3 ceases to be given off (G., *l.c.*). According to Münzig (*l.c.*), the orange-coloured crystalline powder that separates when V_2O_5 is added to boiling conc. H_2SO_4 until the acid is saturated is $V_2O_5 \cdot 2SO_3$. By keeping a solution of V_2O_5 in a large excess of conc. H_2SO_4 at 130° – 150° for a long time, Gerland (*l.c.*) obtained a hard, opaque, sealing-wax red, crystalline crust composed of V_2O_5 and SO_3 in approximately the ratio $V_2O_5 : 2SO_3$.

$V_2O_5 \cdot 2SO_3$ [$= (VO_2)_2SO_4 \cdot SO_3$] is described by G. (*l.c.*) as a clear red, crystalline, deliquescent solid; addition of a drop or two of water ppts. $V_2O_5 \cdot xH_2O$.

Vanadic trisulphate $V_2O_5 \cdot 3SO_3$ (? xH_2O). This salt seems to have been obtained by Berzelius (*l.c.*). Ditte (*C. R.* 102, 757) gave x the value 3; Gerland's analyses (*l.c.*) were inconclusive, the percentage of water found varying from .8 to 7.3. G. (*l.c.*) prepared this salt by long-continued boiling of a solution of V_2O_5 in a large excess of conc. H_2SO_4 ; small crystals separated, some of them brown and some ruby-red and transparent (probably regular octahedra). When the boiling was not continued for so long a time, G. noticed that fine, golden-yellow, lustrous needles separated. The composition of the crystals in each case was very nearly that required by the formula $V_2O_5 \cdot 3SO_3$. More or less $V_2O_5 \cdot 2SO_3$ was always formed; G. found that addition of a little $HClO_4$ prevented the formation of much $V_2O_5 \cdot 2SO_3$.

$V_2O_5 \cdot 3SO_3$ is very deliquescent; soluble in cold water or alcohol; a slight rise of temperature suffices to ppt. $V_2O_5 \cdot xH_2O$. By adding to a solution of this salt in cold water the proper quantity of K_2SO_4 , G. (*l.c.*) obtained small, amber-yellow crystals, which, after a few washings with cold water, pressure between paper, and drying over H_2SO_4 , had the composition of the double salt $V_2O_5 \cdot 2SO_3 \cdot K_2O \cdot 6aq$. The same crystals were obtained by using the disulphate $V_2O_5 \cdot 2SO_3$. Replacement of K_2SO_4 by $(NH_4)_2SO_4$ produced the double salt $V_2O_5 \cdot 2SO_3 \cdot (NH_4)_2O \cdot 4aq$. No double salts were obtained by using Na_2SO_4 or $MgSO_4$, but the trisulphate ($V_2O_5 \cdot 3SO_3$) crystallised unchanged.

Gerland (*B.* 11, 102) found that when a solution of V_2O_5 in hot conc. H_2SO_4 was largely diluted and dialysed, H_2SO_4 passed rapidly through the dialyser, along with small quantities of V compounds, until the liquid in the dialyser contained V_2O_5 and SO_3 in the ratio $V_2O_5 : 8SO_3$, after which SO_3 passed very slowly through, and the composition of the substance in the dialyser gradually approached $V_2O_5 \cdot 2SO_3$. By dialysing a diluted solution of V_2O_5 in cold conc. H_2SO_4 , the conditions being the same as in the experiment with the hot acid, G. found that SO_3 passed through the dialyser regularly, and that, after a time, the ratio of V_2O_5 to SO_3 in the dialyser was 1:1.82. G. supposed these results to mean that a solution of V_2O_5 in cold

H_2SO_4 contains loose, easily decomposed compounds of V_2O_5 and H_2SO_4 , but that a solution of V_2O_5 in hot H_2SO_4 contains $\text{V}_2\text{O}_5 \cdot 3\text{SO}_3$, which gradually loses SO_3 until $\text{V}_2\text{O}_5 \cdot 2\text{SO}_3$ is formed.

Solutions of V_2O_5 in conc. H_2SO_4 may be reduced to sulphates of lower oxides (Roscoe, C. J. [2] 6, 334; Rammelsberg, B. B. 1880, 787):—Zn, Cd, or Na-amalgam causes reduction to lavender solutions of $\text{V}_2\text{O}_5 \cdot x\text{SO}_3$; Mg effects reduction to green solutions of $\text{V}_2\text{O}_5 \cdot x\text{SO}_3$; and H_2S , SO_2 , or oxalic acid reduces only to blue solutions of $\text{V}_2\text{O}_5 \cdot x\text{SO}_3$.

By fusing V_2O_5 with B_2O_3 (Guyard, Bl. [2] 25, 354) obtained a green glass, which he took to be a *vanadic borate*; no analyses or descriptions are given.

The compounds of V_2O_5 with As_2O_3 , I_2O_5 , P_2O_5 , MoO_3 , and WO_3 , respectively—or some of these compounds—may perhaps be regarded as vanadic arsenates, iodates, &c.; v. ARSENO-VANADIC ACIDS AND SALTS, IODO-VANADIC ACIDS, &c., p. 853.

HYPOVANADO-VANADIC OXIDES. Several oxides seem to exist intermediate between V_2O_5 and V_2O_4 . Roscoe noticed that V_2O_5 gradually absorbed O and H_2O from the air, forming a greenish solid; Brierley (C. J. 49, 30) found that a pale grass-green substance was formed after some months, having the composition $\text{V}_2\text{O}_5 \cdot 2\text{V}_2\text{O}_4 \cdot 8\text{aq} = \text{V}_2\text{O}_5 \cdot 4\text{aq}$. By dissolving this solid in dilute $\text{H}_2\text{SO}_4\text{aq}$ and neutralising by KHOaq , B. obtained $2\text{V}_2\text{O}_5 \cdot 4\text{V}_2\text{O}_4 \cdot 6\text{K}_2\text{O} \cdot \text{aq}$. By gently heating the compound $2\text{V}_2\text{O}_5 \cdot 3\text{V}_2\text{O}_4 \cdot 3(\text{NH}_4)_2\text{O} \cdot 6\text{aq}$ (v. HYPOVANADO-VANADATES, p. 853), B. (l.c.) obtained a dark-green solid that absorbed water from the air, and then had the composition $3(\text{V}_2\text{O}_5 \cdot \text{V}_2\text{O}_4) \cdot 8\text{aq} = 3\text{V}_2\text{O}_5 \cdot 8\text{aq}$ (cf. Ditto, C. R. 101, 151; also Manasse, A. 240, 23).

Compounds of SO_3 with oxides intermediate between V_2O_5 and V_2O_4 are formed by the reducing action of zinc on solutions of V_2O_5 in H_2SO_4 (v. Rammelsberg, B. B. 1880, 787).

Vanadium oxyacids, and salts and derivatives thereof. Two oxyacids have been isolated, HVO_3 and $\text{H}_2\text{V}_2\text{O}_7$, corresponding with HPO_3 and $\text{H}_2\text{P}_2\text{O}_7$; salts of these, also salts of the tribasic acid H_2VO_4 , and several more complex salts, are known. Salts derived from the hypothetical hypovanadic acid $\text{V}_2\text{O}_5(\text{OH})_2 (= 2\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O})$ have also been prepared; and several compounds are known which are most simply regarded as $x\text{V}_2\text{O}_5 \cdot y\text{V}_2\text{O}_4 \cdot z\text{MO}$, and which may be called hypovanado-vanadates. V_2O_5 also combines with several acidic and basic oxides simultaneously to form compounds of the general form, $x\text{V}_2\text{O}_5 \cdot y\text{X} \cdot z\text{MO}$; these compounds are generally described as arseno-vanadates, phospho-vanadates &c.

VANADIC ACIDS. Two vanadic acids, HVO_3 and $\text{H}_2\text{V}_2\text{O}_7$, have been isolated; salts of the triacid, H_2VO_4 , are known, but the acid itself has not certainly been prepared.

Metavanadic acid HVO_3 . (Monobasic vanadic acid. Monohydrate of vanadic oxide $\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$.) Gerland (B. 9, 872 [8676]) prepared this acid by adding an excess of NH_4Claq to cold CuSO_4aq , then adding $\text{NH}_4\text{VO}_3\text{aq}$ till a permanent pp. formed, heating to 75° , washing the lustrous yellow scales that slowly separated with dilute $\text{H}_2\text{SO}_4\text{aq}$ and SO_2aq (to remove V_2O_5), then washing with water, and drying at

100° until the smell of NH_3 ceased. Manasse (A. 240, 52) obtained HVO_3 by decomposing conc. solutions of the Ca, Mg, or Sr salt by a little HNO_3aq , and washing the pp. with dilute HNO_3aq , and then with hot water. Metavanadic acid forms golden-yellow crystalline scales; it is unchanged in air; dissolves very slightly in water; insoluble in absolute alcohol; soluble in NH_4aq , KOHaq , or NaOHaq . By adding $\text{NH}_4\text{VO}_3\text{aq}$ to CuSO_4aq , filtering from the pp. that formed, and dialysing for several days, Gerland (l.c. p. 874) obtained a solution in the dialyser of vanadic acid, which remained clear when heated, and on continued evaporation gave a pp. of red amorphous V_2O_5 . Metavanadic acid forms a series of salts (v. METAVANADATES, *infra*).

This compound is used as a colour in place of gold bronze, under the name of *vanadium bronze*. According to Guyard (Bl. [2] 25, 356), the substance commonly known as *vanadium bronze* is really an ammonium vanadate.

Pyrovanadic acid $\text{H}_2\text{V}_2\text{O}_7$. (Tetrabasic vanadic acid. Dihydrate of vanadic oxide $\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$.) This acid is obtained by decomposing a fairly conc. solution of an alkali vanadate of the form $\text{M}_2\text{V}_2\text{O}_7$ or $\text{M}_2\text{V}_2\text{O}_8$ (v. TETRAVANADATES and HEXAVANADATES, p. 852) by HNO_3aq , washing with cold water, and drying in the air (von Hauer, J. pr. 80, 321). According to Ditto (C. R. 101, 638), the red form of V_2O_5 (v. p. 849) absorbs H_2O from the air, forming $\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$, and also $\text{V}_2\text{O}_5 \cdot 5\text{H}_2\text{O}$. Pyrovanadic acid is described as a brown, amorphous powder, resembling $\text{FeO} \cdot \text{H}_2\text{O}$; dried over H_2SO_4 , it is said to lose half its water. Very slightly soluble in water; the solution is clear yellow; it reddens litmus. $\text{H}_2\text{V}_2\text{O}_7$ is insol. in absolute alcohol; it dissolves readily in NH_4aq . For salts of this acid v. PYROVANADATES (p. 852).

VANADATES. The greater number of the vanadates belong to the series (1) MVO_3 , (2) $\text{M}_2\text{V}_2\text{O}_7$, (3) M_2VO_6 , (4) $\text{M}_2\text{V}_2\text{O}_8$, or (5) $\text{M}_2\text{V}_2\text{O}_{10}$. Series (1), (2), and (3) may be called normal salts; the formulae may be written as (1) $\text{M}_2\text{O} \cdot \text{V}_2\text{O}_5$, (2) $2\text{M}_2\text{O} \cdot \text{V}_2\text{O}_5$, and (3) $3\text{M}_2\text{O} \cdot \text{V}_2\text{O}_5$. Series (4) and (5) may be called acid salts; the formulae may be written as (4) $\text{M}_2\text{O} \cdot 2\text{V}_2\text{O}_5$, and (5) $\text{M}_2\text{O} \cdot 3\text{V}_2\text{O}_5$. Acid salts are also known intermediate between series (1) and (4); the chief of these are (6) $3\text{M}_2\text{O} \cdot 4\text{V}_2\text{O}_5 = \text{M}_6\text{V}_4\text{O}_{23}$ ($\text{M}_2\text{O} : \text{V}_2\text{O}_5 = 1:1\frac{1}{2}$), (7) $3\text{M}_2\text{O} \cdot 5\text{V}_2\text{O}_5 = \text{M}_6\text{V}_5\text{O}_{28}$ ($\text{M}_2\text{O} : \text{V}_2\text{O}_5 = 1:1\frac{1}{2}$), and (8) $2\text{M}_2\text{O} \cdot 3\text{V}_2\text{O}_5 = \text{M}_4\text{V}_3\text{O}_{21}$ ($\text{M}_2\text{O} : \text{V}_2\text{O}_5 = 1:1\frac{1}{2}$). A few salts of the form $3\text{M}_2\text{O} \cdot \text{V}_2\text{O}_5 = \text{M}_6\text{V}_2\text{O}_{17}$ ($\text{M}_2\text{O} : \text{V}_2\text{O}_5 = 1:1$) may be called basic salts. Some salts, especially those of Si and Ti, belong to more complex forms.

Roscoe (C. J. [2] 9, 28) has shown that the alkali orthovanadates, M_2VO_6 , or $3\text{M}_2\text{O} \cdot \text{V}_2\text{O}_5$, are easily decomposed in aqueous solution at the ordinary temperature to pyrovanadates, $\text{M}_2\text{V}_2\text{O}_7$, and MOHAq ; but that orthovanadates are formed, rather than meta- or pyro-vanadates, by fusing V_2O_5 with alkali carbonates; further, that aqueous solutions of alkali pyrovanadates are readily decomposed by CO_2 to alkali carbonates and metavanadates.

METAVANADATES $\text{M}'\text{VO}_3$ or $\text{M}_2\text{O} \cdot \text{V}_2\text{O}_5$. Ammonium metavanadate NH_4VO_3 . Obtained by dissolving $\text{V}_2\text{O}_5 \cdot x\text{H}_2\text{O}$ in excess of NH_4aq , warming, and allowing to evaporate.

Forms a white, crystalline crust. Dissolves slowly in cold water, quickly in boiling water. Decomposed by heat, giving V_2O_5 when air is present. According to Berzelius (*P.* 22, 1), when a solution of $V_2O_5 \cdot xH_2O$ in excess of NH_4Aq is allowed to evaporate without having been heated, NH_4VO_3 separates in lemon-yellow crystals (v. B., *l.c.*; Roscoe, *C. J.* [2] 6, 322; Ditte, *C. R.* 102, 918; Norblad, *B.* 8, 126; Wagner, *D. P. J.* 223, 633; Böttger, *C. C.* 1873, 514).

Barium metavanadate $Ba(VO_3)_2 \cdot aq$. A yellowish-white pp.; obtained, along with red crystals, by ppg. NH_4VO_3Aq by $BaCl_2Aq$ (Manasse, *A.* 240, 23). Sl. sol. in water. Loses H_2O when heated to c. 200° (Berzelius; Norblad, *l.c.*).

Potassium metavanadate $KVO_3 \cdot zaq$. Formed by dissolving V_2O_5 in $KOHAq$ in the ratio $V_2O_5 : KOH$. Various hydrates have been obtained as white crystalline solids, melting to a clear yellow liquid, which solidifies to white, lustrous KVO_3 (v. Berzelius, *l.c.*; Ditte, *C. R.* 104, 902, 1061, 1168).

Sodium metavanadate $NaVO_3$. Obtained by Roscoe (*C. J.* [2] 9, 31) by fusing V_2O_5 and Na_2CO_3 in the ratio $V_2O_5 : 2Na_2CO_3$, dissolving in water, crystallising $Na_2V_2O_7 \cdot 18aq$, and passing CO_2 into an aqueous solution of this salt, when $NaVO_3$ crystallised out and Na_2CO_3 remained in solution. Small yellowish-white crystals, probably monoclinic prisms, melting readily and solidifying to a yellow crystalline mass (cf. Norblad, *l.c.*). Hydrates with 2, 4, and 5 H_2O have been obtained (cf. Ditte, *l.c.*).

The other metavanadates that have been prepared are $Cd(VO_3)_2$ (Ditte, *C. R.* 104, 1705); $Ca(VO_3)_2 \cdot 4aq$ (von Hauer, *J. pr.* 69, 385; 80, 824; Manasse, *A.* 240, 23; cf. Roscoe, *C. J.* [2] 9, 32); $Co(VO_3)_2 \cdot 3aq$ (D., *l.c.*; Radau, *A.* 251, 114), forms double salts with KVO_3 (R., *l.c.*); $Pb(VO_3)_2$ (R., *l.c.*; D., *l.c.*); $LiVO_3 \cdot 2aq$ (Ditte, *C. R.* 104, 1168); $Mg(VO_3)_2 \cdot 6aq$ (D., *l.c.*); Manasse, *l.c.*); $Mn(VO_3)_2 \cdot 4aq$ (Radau, *l.c.*); $AgVO_3 \cdot 4NH_3 \cdot 2aq$ (D., *l.c.*); $Sr(VO_3)_2 \cdot 4aq$ (Norblad, *l.c.*; Manasse, *l.c.*); $Zn(VO_3)_2 \cdot 2aq$ (D., *l.c.*).

ORTHOVANADATES $M_2V_2O_7$ or $3M_2O \cdot V_2O_5$.

Potassium orthovanadate K_2VO_7 . Obtained by fusing V_2O_5 with K_2CO_3 ; decomposed by water, giving $KOHAq$ and $K_4V_2O_7$ (Rammelsberg, *B. B.* 1883, 8).

Sodium orthovanadate $Na_2VO_7 \cdot xH_2O$. Roscoe (*C. J.* [2] 9, 39) obtained the salt with $16H_2O$ by fusing V_2O_5 and Na_2CO_3 in the ratio $V_2O_5 : 3Na_2CO_3$, allowing to cool, dissolving in as little cold water as possible, quickly adding excess of conc. alcohol, allowing to stand for some hours, washing the crystals that formed with small quantities of alcohol, and drying on a porous plate over H_2SO_4 in *vacuo* (cf. Czuczajewicz, *A.* 120, 84; Rammelsberg, *B. B.* 1883, 8). Baker (*C. J.* 47, 353) obtained $Na_2VO_7 \cdot xH_2O$ with $x=8(?)$, 10, and 12; he also obtained the double salt $Na_2VO_7 \cdot NaF \cdot 19H_2O$. The crystalline forms are given by B., and the various hydrates, of Na_2VO_7 are shown to be isomorphous with corresponding arsenates and phosphates. Na_2VO_7Aq changes to $Na_4V_2O_7Aq$ and $NaOHAq$; the change occurs slowly at ordinary temperatures, and rapidly at higher temperatures (R., *l.c.*).

The other orthovanadates that have been pre-

pared are $Ca_2(VO_3)_4$, $CaCl_2$ (Hautefeuille, *U. R.* 103, 800; 104, 501); $Pb_2(VO_3)_4$ and $8Pb_2(VO_3)_4 \cdot PbCl_2$ (R., *l.c.*); Ag_2VO_3 (R., *l.c.*); Tl_2VO_3 (Carnelley, *C. J.* 26, 323).

PYROVANADATES $M_2V_2O_7$ or $3M_2O \cdot V_2O_5$.

Barium pyrovanadate $Ba_2V_2O_7$. Obtained, as a white amorphous powder, by adding $BaCl_2Aq$ to freshly-prepared Na_2VO_7Aq , washing, and drying at 100° . The salt is slightly soluble in water (Roscoe, *C. J.* [2] 9, 33).

Potassium pyrovanadate $K_2V_2O_7$. Hard, deliquescent monoclinic prisms, formed by adding $KOHAq$ to KVO_3Aq , rapidly evaporating to a syrup, and placing over H_2SO_4 (Norblad, *B.* 8, 126).

Sodium pyrovanadate $Na_2V_2O_7 \cdot 16H_2O$. Formed by fusing V_2O_5 and Na_2CO_3 in the ratio $V_2O_5 : 2Na_2CO_3$, dissolving, and crystallising; also by exposing Na_2VO_7Aq to air free from CO_2 until addition of alcohol ppts. silky scales ($Na_2V_2O_7$) (Roscoe, *l.c.*, p. 31). White six-sided tables; e. sol. water, insol. alcohol. $Na_2V_2O_7Aq$ is decomposed by CO_2 to Na_2CO_3Aq and $NaVO_3Aq$ (R., *l.c.*).

The other pyrovanadates that have been prepared are $2Ca_2V_2O_7 \cdot 5aq$ (Roscoe, *l.c.*; cf. Ditte, *C. R.* 104, 1705); $Cu_2V_2O_7 \cdot 3aq$ (von Hauer, *l.c.*); $Pb_2V_2O_7$ (Ditte, *l.c.*); $2Pb_2V_2O_7 \cdot PbO$ (Roscoe, *l.c.*); $Li_2V_2O_7 \cdot 6aq$ (von H., *l.c.*); $Mn_2V_2O_7$ (Ditte, *l.c.*); $Ag_2V_2O_7$ (Roscoe, *l.c.*; Ditte, *l.c.*); $Tl_2V_2O_7$ (Carnelley, *C. J.* 26, 323); $Zn_2V_2O_7$ (D., *l.c.*).

TETRAVANADATES $M_4V_4O_{11}$ or $M_2O \cdot 2V_2O_5$ (also called *divanadates*).

Ammonium tetra vanadate $(NH_4)_4V_4O_{11} \cdot zaq$; $x=3$ or 4. Formed by adding a little acetic acid to boiling NH_4VO_3Aq and evaporating *in vacuo*; also by saturating NH_4Aq with V_2O_5 in a closed, warmed flask, and allowing to evaporate; red prismatic crystals with a golden-yellow sheen (Berzelius, *P.* 22, 1; Rammelsberg, *B. B.* 1883, 8; von Hauer, *l.c.*; Ditte, *C. R.* 102, 918).

Potassium tetra vanadate $K_4V_4O_{11} \cdot zaq$; $x=3, 4, 7$, and 10. Obtained by saturating K_2CO_3Aq at 80° with excess of V_2O_5 , and allowing to cool; also by adding acetic acid to V_2O_5 in $KOHAq$, concentrating at 80° , and letting cool (Ditte, *C. R.* 104, 902, 1061, 1168; cf. Norblad, *B.* 8, 126). Orange-coloured tablets (v. also Gibbons, *C. N.* 80, 267).

The other tetra vanadates are $Ca_4V_4O_{11} \cdot 9aq$ (Manasse, *A.* 240, 23); $Pb_4V_4O_{11}$ (Ditte, *l.c.*); $Li_4V_4O_{11} \cdot 9aq$ (Norblad, *l.c.*); $Mg_4V_4O_{11} \cdot 9aq$ (B., *l.c.*; von Hauer, *l.c.*); $Ni_4V_4O_{11} \cdot 3aq$ (Radau, *A.* 251, 114); $Na_4V_4O_{11} \cdot 9aq$ (Berzelius, *P.* 22, 1; von Hauer, *l.c.*; Norblad, *l.c.*); $Sr_4V_4O_{11} \cdot 9aq$ (B., *l.c.*; von H., *l.c.*).

HEXAVANADATES $M_6V_6O_{19} \cdot xH_2O$ or

$M_2O \cdot 3V_2O_5 \cdot xH_2O$ (also called *trivanadates*). These salts have been described by Norblad (*B. B.* 126) and Ditte (*C. R.* 104, 902, 1061, 1168). The chief are those where $M_2 = (NH_4)_2$, Cd , Ca , K , and Na .

The principal vanadates belonging to other series than those already mentioned are the following:—(1) $3M_2O \cdot 4V_2O_5$ ($=M_6H_6V_6O_{22}$), $M=Ca$ and Sr (v. Manasse, *l.c.*); (2) $3MO \cdot 5V_2O_5$ ($=M_3H_3V_3O_{25}$), $M=Ba$, Mg , K , (v. Manasse, *l.c.*; Radau, *A.* 251, 114); (3) $2MO \cdot 3V_2O_5$ ($=M_2H_2V_2O_{17}$), $M=(NH_4)$, Ba , Li , Mg , K , Na (v. Ditte, *l.c.*; also *C. R.* 96,

1048; Manasse, *l.c.*; Norblad, *l.c.*); (4) $4M_2O \cdot V_2O_5$ ($= M_2V_2O_5$), $M = Li$ and Na (*v. Ditte, l.c.*).

Several other vanadates not belonging to any of these series have also been described; for Ca and Sr salts (and double salts), *v. Manasse (l.c.)*; and for Tl salts *v. Carnelley (C. J. 26, 323)*.

HYPOVANADATES. Salts of hypothetical hypovanadic acid $V_2O_5(OH)_2$ ($= 2V_2O_5 \cdot H_2O$). These salts belong to the form $M_2V_2O_5 \cdot xH_2O$ ($= M_2O \cdot 2V_2O_5 \cdot xH_2O$). The formation of the NH_4 and K salts was described by Berzelius; a series of salts was prepared and examined by Crow (*C. J. [2] 15, 458*). The alkali salts are obtained by treating fairly conc. VO_2Cl aq. (*v. Hydrated Vanadium Dioxymonochloride*, p. 854) with excess of caustic alkalis, allowing the pps. to settle in closed vessels, washing with alkali solution, then with dilute alcohol containing a little acetic acid, and finally with alcohol alone, and drying between paper. The salts of Pb and Ag are obtained by ppn. from a solution of the K salt. The salts form brown to black crystalline powders; the alkali salts dissolve in water. Crow prepared salts with $M_2 = (NH_4)_2, Ba, Pb, K, Ag,$ and Na .

HYPOVANADO-VANADATES. Salts of the form $nV_2O_5 \cdot mV_2O_5 \cdot pM_2O \cdot xH_2O$. Alkali salts of this series were obtained by Brierley (*C. J. 49, 32*) by reducing V_2O_5 aq. by SO_2 , adding V_2O_5 in alkali, then a slight excess of alkali, and then acetic acid; pouring into alkali acetate solution, washing the pps. with alcohol, and drying over $CaCl_2$. The salts crystallise in greenish-black, or black, prisms. The following were prepared: (1) $2V_2O_5 \cdot V_2O_5 \cdot 2Na_2O \cdot 0.13H_2O$; (2) $2V_2O_5 \cdot V_2O_5 \cdot 2K_2O \cdot 0.6H_2O$; (3) $2V_2O_5 \cdot 2V_2O_5 \cdot (NH_4)_2O \cdot 0.14H_2O$; these salts are soluble in water: (4) $2V_2O_5 \cdot 4V_2O_5 \cdot 5K_2O \cdot H_2O$; (5) $2V_2O_5 \cdot 4V_2O_5 \cdot 3(NH_4)_2O \cdot 0.6H_2O$; these are insoluble in water.

COMPLEX VANADIC ACIDS AND SALTS. Vanadic oxide V_2O_5 combines with several anhydrides, such as As_2O_3, I_2O_5, P_2O_5 , &c., and many of the compounds thus produced combine with basic oxides. The compounds of V_2O_5 with certain anhydrides are generally regarded as acidic; and the compounds formed of V_2O_5 , anhydrides, and bases are usually classed as salt-like substances. It is quite likely that many of the compounds of V_2O_5 with anhydrides, such as As_2O_3, P_2O_5 , &c., would be better classed as salts, just as the compounds of V_2O_5 with SO_3 are classed as salts.

ARSENO-VANADIC ACIDS AND SALTS. By boiling V_2O_5 with excess of H_3AsO_4 aq. and concentrating the solution, Fernandez (*B. 17, 1632*) obtained lustrous, golden-yellow crystals of $V_2O_5 \cdot As_2O_3 \cdot 11aq$ (*cf. Friedheim & Schmitz-Dumont, B. 23, 2600*). Gibbs (*P. Am. A. 21, 50*) obtained $xV_2O_5 \cdot yAs_2O_3$ aq. (x and y probably either 5 and 8, or 7 and 6), by decomposing a mixture of Na vanadate and arsenate by HNO_3 aq. For various compounds of the form $nV_2O_5 \cdot mAs_2O_3 \cdot pMO$, where m and n are 1 and 1, 2 and 5, 1 and 2, 2 and 1, &c., and p varies from 7 to 5, *v. F. A. S.-D. (l.c.)*.

Iodo-vanadic acids. Ditte (*C. R. 102, 757*) says that compounds of V_2O_5 and I_2O_5 are formed by heating V_2O_5 with conc. HIO_4 aq; he gives formulæ, but no analyses.

MOLYBDO-VANADIC ACIDS AND SALTS. For descriptions of numerous compounds of the forms $xV_2O_5 \cdot yMoO_3$ aq., $xV_2O_5 \cdot yMoO_3 \cdot pMO$ aq., and also $xV_2O_5 \cdot yMoO_3 \cdot mP_2O_5 \cdot pMO$ aq., *v. Gibbs (P. Am. A. 18, 232)*.

PHOSPHO-VANADIC ACIDS AND SALTS. Various compounds of V_2O_5, P_2O_5 , and H_2O are described by Gibbs (*P. Am. A. 21, 50*); Ditte (*C. R. 102, 757*) also assigned formulæ to substances obtained by heating V_2O_5 with conc. H_3PO_4 . Friedheim (*B. 23, 1580*) obtained $V_2O_5 \cdot P_2O_5 \cdot 2H_2O$ by dissolving V_2O_5 in syrupy H_3PO_4 .

For descriptions of a great many compounds of the form $xV_2O_5 \cdot yP_2O_5 \cdot mMO$ aq., *v. Gibbs (l.c.)*; and *cf. Friedheim (l.c.)*.

F. divides the compounds formed by reacting with V_2O_5 on alkali phosphates into two classes, which he calls *luteo-* and *purpureo-* compounds.

Luteo- compounds are formed by (1) the interactions of phosphoric and vanadic acids in solution; (2) the interactions of solutions of phosphates and vanadates in presence of small quantities of acids; (3) the interactions of solutions of phosphates and vanadic acid; (4) the interactions of vanadates and phosphoric acid, by heating solutions nearly to boiling and evaporating. These compounds are yellow, granular, and indistinctly crystalline; the alkali compounds are very slightly soluble in water, solution being accompanied by decomposition. The following luteo- compounds are described by F.: $V_2O_5 \cdot P_2O_5 \cdot 2H_2O$ 9aq., $V_2O_5 \cdot P_2O_5 \cdot (NH_4)_2O \cdot H_2O$ 2aq., $2V_2O_5 \cdot P_2O_5 \cdot (NH_4)_2O$ 7aq., $V_2O_5 \cdot P_2O_5 \cdot K_2O \cdot H_2O$ 2aq. and $2V_2O_5 \cdot P_2O_5 \cdot K_2O$ 7aq.

Purpureo- compounds are formed by dissolving vanadic acid in conc. solutions of alkali phosphates, and by adding phosphoric acid to conc. solutions of alkali vanadates; in each case the solutions should be strongly heated. The purpureo- compounds described by F. belong to the form $12V_2O_5 \cdot P_2O_5 \cdot 7M_2O \cdot 26aq$; they are dark-red crystalline substances, sol. in water.

F. regards the luteo- compound of the form $V_2O_5 \cdot P_2O_5 \cdot 2H_2O$ 9aq as acid phosphate of the radicle VO_2 , thus $(VO_2)_2H_2PO_4$ 9aq; he compares this with the acid orthophosphates MH_2PO_4 . The compounds of the form $V_2O_5 \cdot P_2O_5 \cdot M_2O \cdot H_2O$ aq are looked on as double acid phosphates of alkali metal and VO_2 , thus $NH_4(VO_2)HPO_4$. The luteo- compounds $2V_2O_5 \cdot P_2O_5 \cdot M_2O$ aq are formulated by F. as double compounds of alkali metavanadates and $(VO_2)_2H_2PO_4$; thus $2V_2O_5 \cdot P_2O_5 \cdot K_2O \cdot 2H_2O$ 5aq $= 2(KVO_2 \cdot (VO_2)_2H_2PO_4 \cdot 2\frac{1}{2}aq)$. The purpureo- compounds which belong to the form $12V_2O_5 \cdot P_2O_5 \cdot 7M_2O$ aq are looked on by F. as double compounds of acid vanadates and acid phosphates; this view of their constitution is expressed by the statement

$12V_2O_5 \cdot P_2O_5 \cdot 7M_2O \cdot xH_2O = P_2O_5 \cdot 2M_2O \cdot H_2O + 12V_2O_5 \cdot 5M_2O + (x-1)H_2O$. These views of F. are considerably modified in a later paper (*Zeit. f. anorg. Chemie, 5, 437*), where the purpureo- compounds are looked on as divanadates with some V_2O_5 isomorphously replaced by P_2O_5 . According to F., many of the substances described by Gibbs and by Ditte do not exist.

Berzelius (*P. 22, 1*) described a compound

of V_2O_5 , P_2O_5 , and SiO_2 with H_2O , which may be named *phospho-silico-vanadic acid*.

TUNGSTO-VANADIC ACIDS AND SALTS. The compounds of V_2O_5 with WO_3 and bases that have been described are very numerous, and the formulae given are generally extremely complex (v. Gibbs, *P. Am. A.* 18, 232; Rosenheim, *A.* 251, 197, 234; and especially Friedheim, *B.* 17, 1505; 23, 1505; 24, 1173).

Vanadium oxybromides of. Two compounds of V with O and Br have been isolated; $VOBr_2$ and $VOBr_3$, corresponding with two of the five oxychlorides. According to Schafarik (*N. A. B.* 83, 14; 47 [11] 851), other oxybromides also exist.

VANADIUM OXYDIBROMIDE $VOBr_2$. (*Vanadyl dibromide*.) A brown, deliquescent powder. Prepared by heating $VOBr_3$ (v. *infra*); decomposition to $VOBr_2$ and Br occurs slowly at temperatures below 180° , and suddenly at 180° . Heated in air forms V_2O_5 ; dissolves in water, forming a blue solution (Roscoe, *C. J.* [2] 9, 26). Ditte (*C. R.* 102, 1310) says that a compound $VOBr_2 \cdot 4H_2O$ is formed, as dark-green, deliquescent crystals, by treating red V_2O_5 with HBr. D. writes the formula $V_2O_5 \cdot Br_2 \cdot 2HBr \cdot 7H_2O$.

VANADIUM OXYTRIBROMIDE $VOBr_3$. (*Vanadyl tribromide*.) Prepared by passing vapour of pure Br over V_2O_5 , heated to redness, condensing the yellowish-white vapours that are formed, removing excess of Br from the red liquid by heating to 40° – 50° at c. 100 mm. pressure in a current of perfectly dry air, and then distilling *in vacuo* (Roscoe, *C. J.* [2] 9, 24). $VOBr_3$ is a red, very hygroscopic liquid that boils at 130° – 136° at 100 mm. pressure; S.G. 2.9673 at 0° ; 2.9325 at 14.5° ; decomposes slowly at the ordinary temperature, and suddenly at 180° , to $VOBr_2$ and Br (R., l.c.).

Vanadium oxychlorides of. Five compounds of V with O and Cl have been isolated: $VOCl$, $VOCl_2$, $VOCl_3$, $V_2O_5 \cdot Cl_2$, and $VO_2 \cdot Cl_2$ (zaq.).

VANADIUM OXYMONOCHLORIDE $VOCl$. (*Vanadyl monochloride*.) Obtained by the regulated reduction of $VOCl_3$ by H. The mixed vapours are passed through a red-hot tube; $VOCl$ is deposited near the end whereat the vapours enter the tube. A brown, light, flocculent powder; insol. in water; easily dissolved by HNO_3 (Roscoe, *C. J.* [2] 6, 347).

VANADIUM OXYDICHLORIDE $VOCl_2$. (*Vanadyl dichloride*.) Prepared by heating a slight excess of $VOCl_3$ with zinc for some days in a sealed tube, at 400° , cutting off the part of the tube on which the sublimates of $VOCl_3$ has formed (V_2O_5 and $ZnCl_2$ are the other products), quickly placing it in a wider tube, and removing $VOCl_3$ by heating in a stream of dry CO_2 at 180° . Also obtained by passing vapour of $VOCl_3$ and H through a red-hot tube; $VOCl_2$ is deposited near the end of the tube whereat the gases enter, and $V_2O_5 \cdot Cl_2$ at the further end of the tube (Roscoe, l.c., p. 348). Lustrous, grass-green, deliquescent tablets; S.G. 2.88 at 13° ; slowly decomposed by water; soluble in dilute HNO_3 (Aq.). A compound with $PtCl_4$, having the composition $2(VOCl_2 \cdot PtCl_4) \cdot 21aq.$, is said by Brauner (*M.* 3, 58) to be formed by dissolving V_2O_5 in conc. $HClAq$ in presence of $PtCl_4$ (Aq.).

VANADIUM OXYTRICHLORIDE $VOCl_3$. (*Vanadyl trichloride*.) Mol. w. 173.27.

Formation.—1. By heating V_2O_5 gently in a stream of Cl (Berzelius, *P.* 22, 1).—2. By heating a mixture of V_2O_5 and C in Cl.

Preparation.—A mixture of V_2O_5 and sugar-charcoal is heated to redness in a stream of dry H, and allowed to cool in that gas; a stream of dry Cl is then passed over the mixture, which is heated to redness, and the product is condensed; the liquid thus obtained is heated for some hours in a flask with an inverted condenser, in a current of dry CO_2 , and then rectified over Na (Roscoe, *C. J.* [2] 6, 342).

Properties and Reactions.—A clear, mobile, lemon-yellow liquid (Berzelius, l.c.; Roscoe, l.c.; Schafarik, *A.* 109, 85). S.G. 1.836 at 17.5° ; 1.828 at 24° (R., l.c.); 1.86534 at 0° ; 1.63073 at b.p. (Thorpe, *C. J.* 37, 348). B.P. 127.19° (T., l.c.). S.V. 106.25 . Does not solidify above -15° (R., l.c.). V.D. 88.38 at 186° (R., l.c.; cf. T., *C. N.* 24, 827; Schafarik, l.c.). Gives off thick, yellowish-red fumes in the air. Dissolves in a little water, forming a thick, red liquid; dissolves in much water, forming a clear yellow liquid; dissolves in absolute alcohol with a red colour, but the solution soon becomes blue, owing to reduction. Heated to 60° – 70° in a closed tube with ether forms needles of the composition $VOCl_2 \cdot Et_2O$ (Bedson, *C. J.* 29, 309).

DIVANADIUM DIOXYMONOCHLORIDE $V_2O_5 \cdot Cl_2$. (*Divanadyl monochloride*.) Yellow-bronze, microscopic crystals, resembling mosaic gold; formed by passing $VOCl_3$ and H through a red-hot tube. The crystals are deposited on the part of the tube farthest from the end whereat the gases enter (Roscoe, *C. J.* [2] 6, 348). Insoluble in water; soluble in HNO_3 (Aq.). This compound was thought by Schafarik (*A.* 109, 85) to be V.

HYDRATED VANADIUM DIOXYMONOCHLORIDE $VO_2 \cdot Cl_2$ (zaq.). (*Hypovanadic chloride*.) Formed, as a brown, deliquescent solid, by passing H_2S into a solution of V_2O_5 in hot $HClAq$, filtering from S, and evaporating (Crow, *C. J.* 30, 457). Heated in a stream of dry CO_2 , gives off HCl and H_2O , and leaves V_2O_5 (C. (l.c.) gives the hydration as $V_2O_5 \cdot Cl_2 \cdot 5aq.$

Vanadium oxyfluorides of. No compound of V with O and F has been isolated with certainty. V_2O_5 dissolves in excess of $HFAq$; on evaporation, solution in water, and evaporation over H_2SO_4 , Petersen (*J. pr.* [2] 40, 194) obtained blue, microscopic crystals which he supposed might be VOF_2 (zaq.), inasmuch as a solution of these crystals in $HFAq$ treated with fluorides yielded salts of the form $xMF_2 \cdot yVOF_2$ (v. *HYPOVANADOXYFLUORIDES*, p. 845). F. did not obtain enough of the blue crystals for analysis.

Vanadium oxyiodides of. According to Ditte (*C. R.* 102, 1310), an oxyiodide $2VOI_2 \cdot 9H_2O$ is formed, as a black, deliquescent mass, by adding excess of $HIAq$ to a warm solution of red V_2O_5 , removing free I by shaking with finely-divided Ag, filtering, and evaporating *in vacuo*. The compound is said to react with NH_3 (Aq.), giving $(NH_4)_2VOI_2$. D. writes the formula as $V_2O_5 \cdot I_2 \cdot 2H_2O$; but no analyses are given.

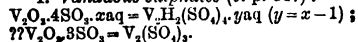
No reaction occurs when I is heated with V_2O_5 (Roscoe, *C. J.* [2] 9, 28); nor when V_2O_5 is digested with water, or alcohol, and I (Guyard,

Bl. [2] 25, 351). V_2O_5 and Li_2O , probably combine (v. Ditte, C. R. 102, 757, 1019).

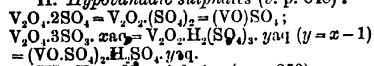
Vanadium, oxy-sulphides of. None of these compounds has been certainly isolated. Oxy-sulphides may perhaps be formed by decomposing alkali thiovanadates in solution by dilute acids (v. Kay, C. J. 87, 728).

Vanadium, salts of. Compounds of the oxides V_2O_5 , V_2O_4 , and V_2O_3 with acidic oxides have been isolated; the formulae of one or two of the compounds may be written as derived from oxyacids by replacing H by V, but it is simpler, and more in keeping with the facts that are known, to represent all the compounds by the general formula $V_2O_5 \cdot yX$, where X is an acidic oxide. The best-studied compounds of V_2O_5 with acidic oxides may be represented as salts of the radicle V_2O_5 (divanadyl), or of the radicle VO (vanadyl); and the compounds of V_2O_4 with acidic oxides as acid salts of the radicle VO_2 . The sulphates have been better studied than the other salts; the following table presents the compositions of the sulphates.

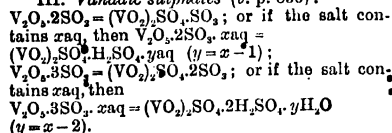
I. *Vanadous sulphates* (v. p. 847):



II. *Hypovanadic sulphates* (v. p. 848):



III. *Vanadic sulphates* (v. p. 850):



Alkalis probably ppt. $V_2O_5 \cdot zaq$ from solutions of vanadous sulphates (v. p. 847); from solutions of hypovanadic sulphates alkalis ppt. $V_2O_4 \cdot zaq$ (v. p. 848).

V_2O_5 dissolves in oxyacids, forming lavender solutions which probably contain $V_2O_5 \cdot xX$, where X is an acidic oxide (v. p. 846).

Various salts of V_2O_5 , V_2O_4 , and V_2O_3 , besides the sulphates probably exist, but they have not been thoroughly examined (v. HYPOVANADIC SALTS, p. 848; VANADIC SALTS, p. 850; ARSENO-VANADIC ACIDS AND SALTS, p. 853; IODO-VANADIC ACIDS, p. 853; MOLYBDO-VANADIC ACIDS AND SALTS, p. 853; PHOSPHO-VANADIC ACIDS AND SALTS, p. 853; and TUNGSTO-VANADIC ACIDS AND SALTS, p. 854).

Vanadium, silicide of. Roscoe (C. J. [2] 8, 358) says that V acts on glass or porcelain vessels when strongly heated therein, forming a compound with Si; tubes in which V chlorides are reduced by heating in H get coated with a grey lustrous mirror of this compound? No details or analyses are given.

Vanadium, silicofluoride of. By boiling V_2O_5 with H_2SiF_6 Aq and alcohol, Guyard (Bl. [2] 40, 352) obtained a greyish, uncrystallisable mass which he took to be a silicofluoride of V; no analyses or details of preparation are given.

Vanadium, sulphides of. Berzelius (P. 22, 1) described two compounds of V and S, one obtained by pptg. a solution of an alkali thiovanadate by dilute acid, and the other by heating V_2O_5 in H_2S . B. gave the formulae VS_2 and

VS , to the compounds he described. The sulphides of V were re-examined by Kay in 1880 (C. J. 87, 728), who found that the pp. obtained by adding dilute HCl Aq or H_2SO_4 Aq to a solution of sodium vanadate saturated with H_2S , or to solution of V_2O_5 in an alkali hydrosulphide, contained O, but probably had not a definite composition; and that the product of heating V_2O_5 in H_2S is the trisulphide V_2S_3 ; Kay prepared three sulphides, V_2S_3 , V_2S_2 , and V_2S , corresponding to three of the four oxides; the sulphides dissolve in solutions of alkali sulphides, probably forming thiovanadates (q. v. infra).

VANADIUM DISULPHIDE V_2S_2 . (*Hypovanadous sulphide*.) Prepared by heating V_2S_3 to full redness, for a long time, in H quite free from O. Forms black lustrous plates, or a brownish-black powder; S.G. 4.2 to 4.4. Absorbs O very quickly when heated in air, giving V_2O_5 , V_2O_4 , and then V_2O_3 , with evolution of SO_2 . Not acted on by boiling HCl Aq, dilute or conc., nor by boiling dilute H_2SO_4 Aq, or cold conc. H_2SO_4 . Dissolves in hot conc. H_2SO_4 ; dissolves in HNO_3 Aq. Slowly acted on by $NaOH$ Aq or KOH Aq, hot or cold; dissolves in $(NH_4)_2SAq$ or $KHSaq$, forming purple to reddish-brown solutions (Kay, l.c. p. 735).

VANADIUM TRISULPHIDE V_2S_3 . (*Vanadous sulphide*.) Formed by strongly heating V_2O_5 in a stream of H_2S (Berzelius, l.c.; Kay, l.c. p. 734); also by heating any chloride of V, or $VOCl_3$, to redness in H_2S (K., l.c.); and by strongly heating V_2O_5 in a stream of vapour of CS_2 so long as any reaction occurs (K., l.c.). Forms dark, lustrous plates, or a black amorphous powder; S.G. 3.7 to 4.0. Oxidised by heating in air, finally to V_2O_5 , giving off SO_2 . Scarcely acted on by dilute HCl Aq or H_2SO_4 Aq, hot or cold, nor by conc. HCl Aq; readily oxidised by HNO_3 Aq. Soluble in $(NH_4)_2SAq$ or $KHSaq$, forming purple-red to golden-red solutions; also somewhat soluble in KOH Aq, $NaOH$ Aq or NH_4OH Aq (Kay, l.c.).

VANADIUM PENTASULPHIDE V_2S_5 . (*Vanadic sulphide*.) Prepared by mixing V_2S_3 with $\frac{2}{3}$ its weight of pure powdered S, heating to fusion (c. 400°) in a narrow tube quite filled with CO_2 and sealed, cooling, and dissolving out excess of S with CS_2 . A black powder; S.G. 3.0. Heated in a gas that does not react with it, V_2S_5 gives off S and leaves V_2S_3 ; heated in air gives off SO_2 , forming V_2O_5 and finally V_2O_3 . Behaves towards acids similarly to V_2S_3 . Dissolves in hot $NaOH$ Aq; also in $(NH_4)_2SAq$ or $KHSaq$, forming yellow to red solutions (Kay, l.c. p. 738).

Vanadium thio-acids, and salts thereof. No compound of V with H and S has been isolated, but some thiovanadates, and also some oxythiovanadates, have been prepared by Krüss a. Ohm (B. 23, 2547).

Ammonium thio-orthovanadate $(NH_4)_2VS_4$. Obtained, in purple crystals, resembling $KMnO_4$, S.G. 1.62, by passing H_2S into a solution of NH_4VO_3 in NH_4 Aq S.G. 898; the solution is saturated in the cold, and is kept cold while H_2S is passed in. A brown pp. is formed, and this dissolves after passing in more H_2S to a dark-violet liquid, from which the salt crystallises after some time.

Sodium monoxo-thio-orthovanadate $Na_2VOB_2 \cdot 5aq$. Obtained by saturating 80 c.c.

NaOHAq S.G. 1.122, with H_2S , adding a solution of 8 g. $\text{Na}_2\text{V}_2\text{O}_7$ in 6 c.c. water, cooling the liquid by ice, and passing in H_2S for 4 hours. The salt was also obtained without water of crystallisation by Krüss (*Zeit. f. anorg. Chemie*, 3, 264) by fusing a mixture of V_2O_5 , Na_2CO_3 , and S, until excess of S was removed. Small crystals, that melt at the ordinary temperature to a red, oily liquid (K. a. O., l.c.).

Sodium trioxo-thio-orthovanadate
 $\text{Na}_2\text{VO}_3\text{S}$. 10aq. Obtained by heating $\text{Na}_2\text{V}_2\text{O}_7\text{Aq}$ to boiling, adding freshly prepared NaSHAq , cooling by ice, and adding alcohol. A red oil, that solidifies to a crystalline mass which melts at 18° (K. a. O., l.c.).

Ammonium monoxo-thio-pyrovandate
 $(\text{NH}_4)_2\text{VO}_3\text{S}$. Formed by passing H_2S into a cooled solution of NH_4VO_3 in NH_4Aq S.G. greater than .898, and allowing the liquid to stand for some months, when crystals separate having S.G. 1.715 (K. a. O., l.c.).

Potassium monoxo-thio-pyrovandate
 KVVO_3S . 3aq. Obtained by passing H_2S into KVO_3 in KOH Aq S.G. 1.472, air being excluded and the liquid cooled by ice. Crystals resemble KMnO_4 ; S.G. 2.144; loses all water slowly at 150° . By evaporating the mother-liquor from this salt *in vacuo*, large crystals of the salt $2\text{KVVO}_3\text{S}$. 3aq are obtained (K. a. O., l.c.).

M. M. P. M.

VANADOXYFLUORIDES and *Hypovanadoxyfluorides*; v. pp. 844-5.

VANADYL COMPOUNDS; compounds of the radicle VO: v. VANADIUM OXYBROMIDES (p. 854), VANADIUM OXYCHLORIDES (p. 854), and HYPOVANADIC SALTS (p. 848).

VANILLIC ACID v. Methyl derivative of PROTOCATECHUIC ACID.

VANILLIN v. Methyl derivative of PROTOCATECHUIC ALDEHYDE.

VANILLO-DIACETONAMINE v. ACETONAMINE.

VAPOUR DENSITIES. The term 'vapour density' is now generally employed to signify the specific gravity of a gas referred to hydrogen as unity. For descriptions of the principles of the methods used in determining vapour densities, v. DENSITIES, RELATIVE, vol. ii. p. 374; and for an account of the application of vapour densities to finding molecular weights, v. ATOMIC AND MOLECULAR WEIGHTS, vol. i. p. 340.

VEGETABLE PROTEIDS v. PROTEIDS.

VERATRALBINE v. JERVINE.

VERATRIC ACID v. Di-methyl derivative of PROTOCATECHUIC ACID.

Homo-veratric acid v. DI-OXY-PHENYL-ACETIC ACID.

VERATROLE v. Di-methyl ether of PYROCATECHIN.

VERATRUM ALKALOIDS.

Veratrine $\text{C}_{22}\text{H}_{33}\text{NO}_7$, v. *Cevadine*. [205°]. S. 12 at 15° . Occurs in the seeds of *Veratrum Sabadilla* (Meissner, N. J. T. 5, 3; Pelletier & Caventou, A. Ch. [2] 14, 69; Cœurbe, A. Ch. [2] 52, 862; Merck, A. 95, 200; Ger. Ph. 231, 135; Delondre J. Ph. [3] 27, 417; Weigelin, O. C. 1873, 259; Schmidt, Ar. Ph. [3] 10, 611; B. 9, 1115; A. 185, 224). Occurs also in the root of *Sarracenia purpurea* (St. Martin, Z. [2] 2, 442; Hétet, C. R. 85, 185). Prepared by extracting

the seeds with boiling alcohol containing a little tartaric acid, concentrating the extract, adding water, filtering from resin, adding Na_2CO_3 , and shaking with ether. The ethereal solution is shaken with dilute tartaric acid solution, and the acid solution mixed with Na_2CO_3 , and extracted with ether. The ethereal extract is mixed with ligroin and allowed to evaporate spontaneously, when a viscid mass first separates, followed by crystals which are recrystallised from alcohol (Wright & Luff, C. J. 33, 838). If commercial veratrine [144°] be dissolved in alcohol at 70° , water added till turbidity ensues, and the solution evaporated at 50° to 60° , crystalline veratrine separates first, then a resinous mixture of veratrine and veratridine, while the mother-liquor contains veratridine and veratroin veratrate (Rosetti, Ar. Ph. [3] 21, 81).

Properties.—Needles (from alcohol), sol. ether, insol. water. Inactive to light. Very poisonous, a small quantity producing vomiting and purging. Introduced into the nose it produces sneezing. Alkaline to test papers. Conc. H_2SO_4 forms a yellow colour changing to crimson, 1 pt. colouring 3,000 pts. H_2SO_4 (Vasmer, Ar. Ph. 2, 74). Conc. HClAq forms a violet solution on warming. HNO_3 forms a red solution, becoming yellow. Veratrine mixed with sugar (3 pts.) is coloured by H_2SO_4 dark green and finally deep blue (Weypen, Fr. 13, 454). A solution of ammonium selenite (1 g.) in H_2SO_4 (20 c.c.) gives a yellow colour at 30° ; in 3 hours a red pp. is formed, the liquid remaining yellow (Da Silva, C. R. 112, 1267). On heating with alcoholic potash or barytes it yields angelic acid and cevine (W. a. L.; Rosetti; Stransky, M. 11, 482). ICl forms a yellow flocculent pp., sol. hot HClAq (Dittmar, B. 18, 1612). Conc. HClAq yields tiglic acid. Veratrine yields tiglic acid and (8)-methyl-pyridine on distillation. On distilling veratrine with lime the products are (8)-methyl-pyridine and Ks hexahydrate and isobutyric acid (Ahrens, B. 23, 2705). Veratrine is not affected by boiling dilute H_2SO_4 .

Salts.— B' HCl . Amorphous.— $\text{B' H}_2\text{P}_2\text{Cl}_4$: amorphous.— B' H AuCl_4 . Yellow needles (from alcohol).— B' H AuCl_4 2aq (Rosetti, J. 1883, 1351).— B' H HgCl_2 . Crystalline pp. v. sol. alcohol.— $\text{B' H}_2\text{SO}_4$ (dried at 100°).— B' HCl . Reddish-brown amorphous solid (Bauer, J. 1874, 861).

Benzoyl derivative $\text{C}_{22}\text{H}_{33}\text{BzNO}_7$. [170°-180°]. Brown crystals (containing $1\frac{1}{2}$ aq) (from ether).— B' H AuCl_4 .

Dibromide $\text{C}_{22}\text{H}_{33}\text{Br}_2\text{NO}_7$. Formed by allowing the tetrabromide to stand in contact with dilute KOH Aq . Light-yellow amorphous solid.

Tetrabromide $\text{C}_{22}\text{H}_{33}\text{Br}_4\text{NO}_7$. Formed by shaking veratrine with bromine-water. Yellow amorphous powder, insol. water, v. sol. alcohol, hard ether (Ahrens, B. 23, 2701).

Cevine $\text{C}_{22}\text{H}_{33}\text{NO}_7$ (W. a. L.); $\text{C}_{22}\text{H}_{33}\text{NO}_7$ (Rosetti). *Cevadine*. [145°] (W. a. L.); [182°-185°] (R.). Formed by boiling veratrine with alcoholic NaOH (W. a. L.). Yellow resin, v. sol. alcohol, sl. sol. ether. Its aqueous solution becomes turbid on warming. Does not attack the mucous membrane, gives a crimson colour with H_2SO_4 , and a brown colour with cane-sugar and H_2SO_4 . Its salts are amorphous.— B' H HgI_2 (dried at 100°). Precipitate.

Veratridine $C_{27}H_{45}NO_{11}$ (W. a. L.); $C_{27}H_{45}NO_{11}$ (Rosetti). *Veratrine*. [180° cor.] (W. a. L.); [160°-165°] (R.). S. 3 at 15°. If the viscid mass which separates before veratrine when a solution of the crude base in alcohol-ligroin is evaporated be shaken with ether, cevadilline remains undissolved, while veratridine dissolves in the ether (Wright a. Luff). Amorphous resin, sl. sol. ether. Decomposed by alcoholic potash into veratric acid and verine $C_{27}H_{45}NO_{11}$ [c. 95°] (W. a. L.) or veratrin $C_{27}H_{45}NO_{11}$ [143°-148°] (R.), an amorphous base, sol. ether. Veratridine dissolves in boiling water, being converted into veratrin veratrate $C_{27}H_{45}N_2O_{11}C_2H_5O_2$ 2aq (Rosetti), which melts, when anhydrous, at 165°-170°. H_2SO_4 forms a yellow solution which turns crimson.—Salts.— $B^+HAuCl_4^-$. Amorphous.— $D^+H_2SO_4$ 10aq, crystalline.

Cevadilline $C_{27}H_{45}NO_{11}$. Obtained as above (W. a. L.). Amorphous, sl. sol. ether, m. sol. benzene. Decomposed by alcoholic potash.

Salts.— $B^+HAuCl_4^-$.— $B^+HHgCl_4^-$. Gelatinous. Cevadilline is perhaps identical with the sabadilline $C_{27}H_{45}N_2O_{11}$ of Wiegelin (C. C. 1872, 229), to which Hesse (A. 192, 186) assigns the formula $C_{27}H_{45}NO_{11}$; while sabatrine $C_{27}H_{45}N_2O_{11}$ (W.) or $C_{27}H_{45}NO_{11}$ (H.) was probably a mixture of decomposition-products (Wright a. Luff).

Veratrum album. The alkaloids in the root of this plant, and in that of *V. viride*, are described under JERININE.

VERATRUMIC ACID IS VERATRIC ACID.

VERINE v. VERATRUM ALKALOIDS.

VERININ $C_{27}H_{45}N_2O_{11}$ 3aq. Occurs in young vetch plants (*Vicia sativa*), in young red clover (*Trifolium pratense*), in pumpkin seeds, in ergot, and in the blossom of *Corylus avellana* and *Pinus sylvestris* (K. Schulze, J. pr. [2] 32, 447; H. 10, 80, 326). Separated from asparagin by crystallisation from hot water. Minute silky prisms, v. sol. hot water, insol. alcohol. Its aqueous solution is neutral, gives no pp. with $Pb(OAc)_2$, but is ppd. by $AgNO_3$, by picric acid, and by phosphotungstic acid in presence of HCl. Boiling hydrochloric acid forms guanine.— $Ag_2C_{27}H_{45}N_2O_{11}$. Gelatinous pp.

VERNONIN $C_{27}H_{45}O_{11}$. Occurs in the root of *Vernonia nigritiana*, used on the west coast of Africa as a febrifuge (Heckel a. Schlagenhaufen, C. R. 106, 1446). White powder, sl. sol. ether and chloroform, sol. alcohol. Conc. H_2SO_4 gives a brown colour, changing to purple. Cardiac poison, 80 pts. being required to produce the effect of 1 pt. of digitalin. Decomposed by boiling dilute HCl into glucose and a resin $C_{27}H_{45}O_{11}$.

VICIN $C_{27}H_{45}N_2O_{11}$. S. 1 at 23°. Occurs in the seeds of *Vicia sativa*, *V. Faba*, and *V. Faba minor* (Ritthausen, J. pr. [2] 2, 333; 24, 202; 29, 359). Obtained by extracting the seeds with cold dilute H_2SO_4 (1:50), neutralising with lime, filtering from $CaSO_4$, evaporating to dryness and crystallising from 85 p.c. alcohol. The yield is 25 p.c.

Properties.—Tufts of small needles, nearly insol. alcohol. Loses $2H_2O$ at 160°. Sol. alkalis and alkaline earths, reppd. on neutralisation. Not affected by boiling baryta-water. Sol. dilute HCl and H_2SO_4 , but after boiling the solution gives a deep-blue colour with $FeCl_3$, and

NH_3 , and a violet pp. with baryta. Boiling KOHAq (S.G. 1.1) also forms divicin. When evaporated with HNO_3 (S.G. 1.2) the residue is edged with deep violet. Potash-fusion forms KCy.

Salts.— $B^+4H_2SO_4$.— B^+11HCl . Slender needles.

Divicin $C_{27}H_{45}N_2O_{11}$. By boiling vicin with water (5 p.c.) containing H_2SO_4 (1 pt.) at 0° there is formed crystalline $(C_{27}H_{45}N_2O_{11})_2SO_4$, which yields divicin on treatment with exactly the calculated quantity of KOHAq. Flat prisms (from water). Reduces $AgNO_3$ at once. Not red. by baryta. A little $FeCl_3$ followed by NH_3 gives a splendid blue colour. B^+SHNO_3 . Wheat-stone-shaped crystals, got by adding HNO_3 to a solution of divicin.

Convicin $C_{27}H_{45}N_2O_{11}$ 2aq. Obtained from powdered vetch seeds by extracting with alcohol, allowing vicin to crystallise from the extract, ppg. the mother-liquor with $HgCl_2$ and potash, decomposing the pp. with aqueous H_2S , and evaporating. The mixture of vicin and convicin so obtained is treated with dilute H_2SO_4 , which dissolves the vicin only. Thin plates (from water), often resembling leucine. Hardly sol. cold water, sl. sol. alcohol. Not decomposed by boiling KOHAq (S.G. 1.1). Potash-fusion gives off NH_3 , but forms no KCy. Insol. cold dilute HCl and H_2SO_4 . Its aqueous solution gives a flocculent pp. with $Hg(NO_3)_2$.

VINACONIC ACID v. TRI-METHYLENE D-CARBOXYLIC ACID.

VINCETOXIN $C_{27}H_{45}O_{11}$ [59°]. $[a]_D = -50^\circ$. Extracted by milk of lime from powdered asclepias root (Tanret, C. R. 100, 277; H. [2] 43, 620). Occurs in two forms, one soluble and one insoluble in water. Both forms are levorotatory, amorphous, sl. alcohol, insol. ether. Boiling dilute HCl yields an amorphous, inactive sugar, which does not ferment with yeast.

VINYL ALCOHOL $CH_2=CH.OH$. This substance might be expected to be identical with aldehyde CH_3CHO , but Poleck a. Thümmel (B. 22, 2863) suppose it to be present in ether that has been exposed to air and sunlight, and that its presence is indicated by the formation of a pp. $C_2H_5OH.HgO.HgCl_2$ when a solution of mercury oxychloride in Na_2CO_3 aq is added to commercial ether. This pp. is white, and is converted by boiling potash into explosive greenish-black 'acetylene mercury' $C_2H_2O.Hg$, and by adding nitric acid to its alkaline solution into $C_2H_3HgOCl_2$, which is not explosive. H_2S passed into water containing the compound $C_2H_2O.HgCl_2$ yields (γ)-tri-thio-acetic aldehyde [76°].

VINYL-DIACETONAMINE v. ACETONAMINES.

VINYL-AMINE $CH_2=CH.NH_2$. Formed by the action of moist Ag_2O or of KOHAq on bromo-ethylamine hydrobromide at 48° (Gabriel, B. 21, 1049, 2655). Known only in aqueous solution. Volatile with steam. Decomposes in aqueous solution even in the cold. SO_2 converts it into taurine.

Salts.— B^+HCl . Poisonous. Its aqueous solution is decomposed by heat.— B^+3PiCl_4 . Crystals, v. sol. water.— B^+2BiCl_3 . Minute scarlet hexagonal leaves.— B^+HAuCl_4 . Golden crystals.— $B^+C_2H_5N_2O_{11}$ [142°]. Slender yellow needles.

References.—DI-iodovinylamine.

VINYL BROMIDE v. Bromo-ethylene.

Vinyl tribromide v. Tri-bromo-ethane.

VINYL CHLORIDE v. Chloro-ethylene.

VINYL ETHANE v. Butylene.

VINYL-ETHYL-CARBINOL, v. PENTENYL ALCOHOL.

VINYL-ETHYLENE v. Butene.

VINYL ETHYL OXIDE $\text{CH}_2\text{CH}_2\text{OEt}$. (35.5° i.v.). S.G. $\frac{14.5}{17.5}$ 7625. Formed by heating chloro-acetal $\text{CH}_2\text{ClCH}_2\text{OEt}$, with sodium at 140° (Wialicenus, A. 192, 106). Liquid, smelling like ether mixed with allyl compounds.* Combines with Cl and Br, forming di-chloro- and di-bromo-di-ethyl oxide. A small quantity (1 g.) of iodine converts large quantities of the oxide (200 g.) into a viscid liquid. Dilute (1:4) H_2SO_4 , forms aldehyde and EtHSO_4 .

Reference.—CHLORO-VINYL-ETHYL OXIDE.

VINYL-ETHYL-PYRIDINE

$\text{C}_4\text{H}_5\text{NEtCH}_2\text{CH}_2$. (98°-102° at 21 mm.). Formed by heating $\text{C}_4\text{H}_5\text{NEtCH}_2\text{CH}_2\text{OH}$ with conc. HCl at 170° (Prausnitz, B. 25, 2394). Oil, v. sol. ether.— $\text{B}^*\text{H}_2\text{PtCl}_6$. Needles, sl. sol. hot water.

VINYL IODIDE v. Iodo-ethylene.

VINYL-MALONIC ACID v. TRIMETHYLENE DICARBOXYLIC ACID.

VINYL OXIDE $(\text{C}_2\text{H}_3)_2\text{O}$. (39°). Formed by the action of dry Ag_2O on vinyl sulphide (Semmler, A. 241, 90).

Reference.—HEXA-CHLORO-DI-VINYL OXIDE.

o-VINYL-PHENOL $\text{CH}_2\text{CH}(\text{C}_6\text{H}_4)\text{OH}$.

Methyl ether $\text{CH}_2\text{CH}(\text{C}_6\text{H}_4)\text{OMe}$. *o*-Vinyl-anisole. (c. 198°). S.G. $\frac{1.5}{1.0095}$ 1-0095. Formed from either of the methyl derivatives of *o*-oxy-phenyl-acrylic acid by successive treatment with HI and Na_2CO_3 (Perkin, C. J. 83, 211; 39, 429). Oil. Polymerises readily (at 150°), forming a glassy mass, which, however, on distillation, regenerates the original oil. It smells like high-boiling coal-tar naphtha. It forms a colourless compound with bromine. Forms a red solid with H_2SO_4 .

p-Vinyl-phenol. **Methyl ether** $\text{CH}_2\text{CH}(\text{C}_6\text{H}_4)\text{OMe}$. [3°]. (205°). S.G. $\frac{1.5}{1.0029}$; $\frac{1.5}{1.0095}$. Formed by distilling methoxy-phenyl-acrylic acid (q.v.) and from the same acid by successive treatment with conc. HI (S.G. 1.94) and Na_2CO_3 .

Reference.—BROMO- and NITRO-VINYL-PHENOL.

VINYL-PIPERIDINE $\text{C}_4\text{H}_9(\text{C}_2\text{H}_5)_2\text{N}$ (?). (147°). Formed by dehydration of oxy-ethyl-piperidine [32°] (Ladenburg, B. 22, 2587). Liquid, smelling like tropidine and coniine, v. sol. water.

Reference.—BROMO-VINYL-PIPERIDINE.

p-VINYL-ISOPROPYL-BENZENE $\text{C}_{11}\text{H}_{14}$, i.e. $\text{C}_6\text{H}_5\text{PrCH}_2\text{CH}_2$. (204°). S.G. $\frac{1.5}{1.002}$ 8902. Formed by distilling cumyl-acrylic acid at 219° or by boiling α -bromo- β -cumyl-propionic acid with Na_2CO_3 (Perkin, C. J. 1877, ii. 660). Oil, smelling like cunfinc aldehyde. Partially polymerises on boiling, and also on keeping, forming a glassy mass, reconverted into the original hydrocarbon by heat. Yields $\text{C}_{11}\text{H}_{11}\text{Br}$ [71°].

a-VINYL-PYRIDINE $\text{C}_6\text{H}_5\text{N}$ i.e.

$\text{N} \begin{smallmatrix} \text{C}(\text{C}_6\text{H}_5)_2\text{OH} \\ \text{CH} \end{smallmatrix} \text{CH} \text{CH}_2$. (159°). S.G. 2 9985. Formed by passing a mixture of pyridine and

ethylene through a red-hot tube (Ladenburg, B. 20, 1648). Formed also by distilling oxy-ethyl-pyridine under high pressure or in presence of KOH (Ladenburg, B. 22, 2585), and by the action of NaOHAq on β -bromo- β -pyridyl-propionic acid (Einhorn, A. 265, 229). Liquid smelling like conyryne, m. sol. water, v. sol. alcohol. Decomposed by distillation under atmospheric pressure, but boils at 81° under 29 mm. Oxidised by KMnO_4 to picolinic acid, and reduced in alcoholic solution by Na to ethyl-pyridine.—Salts: $\text{B}^*\text{H}_2\text{PtCl}_6$. [174°]. Crystals, m. sol. water.— B^*HAuCl_4 . [144°]. Yellow needles.

Tetra-vinyl-pyridine $\text{C}_4\text{H}(\text{C}_2\text{H}_5)_3\text{N}$. (277°). S.G. 2 10515. Formed in the preparation of γ -ethyl-pyridine by heating pyridine ethylo-iodide in sealed tubes at 320° (Karan, B. 25, 2776). Sl. sol. water.— $\text{B}^*\text{H}_2\text{PtCl}_6$. [175°].— B^*HAuCl_4 . [148°].— B^*HHgCl_2 . [146°]. Needles.

VINYL-QUINOLINE v. QUINOLYL-ETHYLENE.

VINYL SULPHIDE $\text{C}_2\text{H}_5\text{S}$ i.e. $\text{S}(\text{CH}_2\text{CH}_2)_2$. (101°). S.G. 913. Constitutes the chief part of the essential oil of *Allium ursinum* (Semmler, A. 241, 90). Liquid, smelling like allyl sulphide.

Reactions.—1. Dry Ag_2O forms vinyl oxide.—2. Moist Ag_2O gives aldehyde.—3. Alcoholic HgCl_2 forms crystals of $\text{C}_2\text{H}_5\text{ClHgS}$, which, when heated with potassium sulphocyanide, yields vinyl sulphocyanide.—4. PtCl_4 added to its alcoholic solution ppts. $(\text{C}_2\text{H}_5)_2\text{Cl}_2\text{PtS}_2$, which is decomposed by ammonium sulphide into vinyl chloride and dark-brown $(\text{C}_2\text{H}_5)_2\text{PtS}_2$.—5. AgNO_3 forms $(\text{C}_2\text{H}_5)_2\text{SAgNO}_3$.—6. Br gives $(\text{C}_2\text{H}_5)_2\text{SBr}_2$. [95°].—7. **Oxidising agents** yield CO_2 , oxalic acid, and H_2SO_4 only.

VINYL-TOLUIDINE so called is **Br-p-TOLYL-DI-ETHYLENE-DIAMINE**.

VIOLAQUERCITRIN v. this vol. p. 873.

VIOLANTIN $\text{C}_8\text{H}_8\text{N}_2\text{O}$, 4aq. Formed by mixing hot conc. solutions of nitroso- and nitro-barbituric acids (violuric and diluturic acids). Formed also by warming hydruilic acid with dilute HNO_3 (Baeyer, A. 127, 223). Yellowish-white, crystalline powder, decomposed by water into its two component acids, but may be recrystallised from HOAc or 50 p.c. alcohol. It is also split up into its components by salts of the stronger acids.

VIOLURIC ACID $\text{C}_4\text{H}_2\text{N}_2\text{O}_4$, i.e.

$\text{C}_2\text{O}_2 \begin{smallmatrix} \text{NH} \\ \text{NH} \end{smallmatrix} \text{C:NOH} \cdot \text{Nitroso-barbituric acid}$. Mpl. v. 157.

Formation.—1. From hydruilic acid by the action of nitric acid (S.G. 1.2) or nitrous acid (Baeyer, A. 127, 200).—2. By heating diluturic (nitro-barbituric) acid with glycerin.—3. By warming ferrous diluturate with KCy .—4. By boiling an aqueous solution of alloxantin with hydroxylamine hydrochloride (Pellizzari, G. 17, 258).—5. By adding hydroxylamine to an aqueous solution of alloxan (Ceresole, B. 16, 1133).—6. By adding KNO_3 to barbituric acid (Baeyer, A. 130, 140).

Properties.—Trimetric crystals (containing aq); a:b:c = 83:1:1.92. M. sol. cold water, sl. sol. alcohol. Its aqueous solution is ppd. by alcohol. FeSO_4 gives a deep indigo-blue colour. HNO_3 forms nitro-barbituric acid. Br forms di-bromo-barbituric acid and nitrous fumes. Reducing agents form uranil (amido-barbituric

acid). Conc. HClAq forms hydroxylamine on heating.

Salts.— $\text{NH}_4\text{A}'$. Dark-blue prisms.— $\text{KA}'2\text{aq}$. Deep-blue crystals, v. sol. water, forming a blue solution; turned red by excess of KOH. A solution of the K salt in conc. HClAq deposits ($\text{KA}'\text{HCl}$), 6aq. in colourless efflorescent prisms.— BaA' , 4aq. Red dimetric tables, nearly insol. cold water.— MgA' , 6aq. Purple-red crystals.— PbA' , 4aq. Small red crystals.— AgA' .

• **Benzyl ether** $\text{C}_6\text{H}_5\text{CH}_2\text{O} < \begin{smallmatrix} \text{NH.CO} \\ \text{NH.CO} \end{smallmatrix} > \text{C.NOC}_6\text{H}_5$. [226°]. Formed by the action of benzyl chloride on silver viridate (Conrad a. Guthzeit, *B.* 15, 2849). Silvery scales, sol. hot water and alcohol.

• **VIRIDIC ACID** v. CAFFEYANIC ACID.

• **VIRIDINE** $\text{C}_{12}\text{H}_{15}\text{N}$. (251°). S.G. 1.024. A homologue of pyridine occurring in coal-tar (Thienius, *C. C.* 1862, 53). Yellowish oil, with slight greenish fluorescence, sl. sol. water, v. sol. alcohol and ether.— $\text{B}'\text{H}_2\text{PtCl}_6$. Greenish brown, insol. water, alcohol, and ether. The mercuric chloride double salt melts at 85° and crystallises from water.

Isomeride $\text{C}_{12}\text{H}_{15}\text{N}$. (230°–235°). Obtained, with other bases, by heating methyl-ethyl-acrolein with alcoholic ammonia (Hoppe-Seyler, *M.* 9, 651).— $\text{B}'\text{H}_2\text{AuCl}_4$. (93°).— $\text{B}'\text{H}_2\text{PtCl}_6$. (135°).

• **VISCIN** $\text{C}_{10}\text{H}_{11}\text{O}_4$ (?). The glutinous constituent of the stalk, leaves, and berries of the mistletoe (*Viscum album*). Extracted from the bark by kneading with water, washing the sticky mass with 90 p.c. alcohol, and extracting the viscin with cold ether. The residue consists of viscacouchin and woody-fibre (Reinsch, *C. C.* 1861, 146). Colourless, tasteless, semi-fluid mass, S.G. 1.0, decomposed by distillation, yielding oily viscene (226°) S.G. .85, which forms a crystalline Na salt with conc. NaOH aq. Viscacouchin is very glutinous. Its S.G. is

.978, and it is insol. alcohol and ether, sol. oil of turpentine.

VISCOSE is DEXTRANE (q. v.).

VITELLIN v. PROTEIDS.

VITELLOSE v. PROTEIDS.

VOLUMES, SPECIFIC; v. SPECIFIC VOLUMES, p. 498.

• **VULPIC ACID** $\text{C}_{12}\text{H}_{11}\text{O}_5$, i.e.

$\text{CPh}(\text{COOH})\text{CPh.CO}_2\text{Me}$. *Methyl pulvate*. $\text{CO} \rightarrow \text{O}$

[148°]. Occurs in *Cetraria vulpina*, a lichen growing in Norway, and used there, mixed with nuxvometa, as poison for wolves (Bebert, *A.* 2, 342; Strecker a. Möller, *A.* 113, 56; Spiegel, *B.* 13, 1629; 14, 1686; *A.* 219, 15). The lichen contains 2½ to 4 p.c. of the acid, which may be extracted by warm milk of lime. Vulpic acid is also formed by dissolving pulvic anhydride in a solution of KOH in MeOH. It appears to occur in the lichen *Parmelia parietina* (Berzelius; Stein, *J.* 1864, 553).

Properties.—Yellow plates or needles, sol. alcohol and ether, v. c. sol. chloroform, nearly insol. boiling water. Decomposed above 200° in MeOH and pulvic anhydride. Boiling milk of lime converts it into pulvic acid. Boiling KOH aq. forms di-benzyl-glycollic acid and CO_2 .

Salts.— $\text{NH}_4\text{A}'$. Yellow crystals, sol. water.— BaA' , 2aq. Yellow needles (from water).— BaA' , 7aq.— KA' aq. Light-yellow needles, sl. sol. water.— AgA' . Pp. Blackens at 190°.

Acetyl derivative $\text{C}_{10}\text{H}_{11}\text{AcO}_4$. [156°]. Colourless needles, insol. NaOH aq.

Methyl ether v. Di-methyl ether of Pulvic acid.

Isovulpic acid $\text{C}_{12}\text{H}_{11}\text{MeO}_5$. [124°]. Formed, in small quantity, together with pulvic anhydride, by heating vulpic acid at 200° (Spiegel). Thin golden plates (from alcohol). Forms orange solutions in alkalis.

W

• **WACKENRODER'S SOLUTION.** The solution obtained by passing H_2S for a long time into nearly saturated SO_2 aq. The solution contains $\text{H}_2\text{S}_2\text{O}_8$, much $\text{H}_2\text{S}_2\text{O}_5$, $\text{H}_2\text{S}_2\text{O}_4$, and probably $\text{H}_2\text{S}_2\text{O}_3$, along with H_2SO_4 , dissolved colloidal S, and a little S in suspension; v. **TRONIC ACIDS**, p. 698.

• **WALDIVIN** $\text{C}_{18}\text{H}_{21}\text{O}_{10}$. [230°]. S.G. 1.46. i. 17 at 15°; 8 at 100°. S. (alcohol) .53. Extracted by dilute alcohol from the powdered fruit of *Simaba waldivia* (Tanret, *Bl.* [2] 35, 191; *J. R.* 91, 886). Hexagonal prisms (containing 2q.), v. sol. chloroform, insol. ether. Neutral to litmus. Inactive to light. Tastes bitter.

• **WATER.** H_2O . (*Hydrogen monoxide*). Mol. w. 17.96. (For physical data v. **Properties**.)

Occurrence.—Pure water is never found in nature. The properties of different specimens of naturally occurring waters depend on the impurities they contain, and these impurities are derived from the substances with which the water has come into contact; hence it is customary to classify natural waters in accordance with their origin, as *rain-water*, *surface-water*,

well-water, *mineral spring-water*, and *sea-water*. The composition of the substances found in these waters, and the properties of the waters themselves—that is, of the various more or less dilute aqueous solutions—are discussed in pp. 983–960 of vol. iv. of the **DICTIONARY OF APPLIED CHEMISTRY**. Solid water, more or less pure, is found as ice and snow. Water vapour is a constant constituent of the atmosphere. A great many minerals, and also many organic substances, contain water combined with other compounds.

Historical.—In 1781 Cavendish showed experimentally that water was the only product of burning H and O mixed in certain proportions, and that almost the whole of the H and O disappeared. The account of the experiments made by Cavendish, was published in 1784 (*T.* 1784, 116).

*When a mixture of inflammable and dephlogisticated air (i.e. in modern language, hydrogen and oxygen) is exploded in such proportions that the burnt air is not much phlogisticated, the condensed liquor contains a little acid, which is always of the nitrous kind . . . ; but if the proportions be such that the burnt air is almost entirely phlogisticated, the condensed liquor is not at all acid, but

came pure water, without any addition whatever; and as, when they are mixed in that proportion, very little air remains after the explosion, almost the whole being condensed, it follows that almost the whole of the inflammable and dephlogisticated air is converted into 'pure water' (*l.c.* p. 183).

Translated into modern language, this statement would be taken as asserting that water is formed by exploding a mixture of H and O in proper proportions. It is, however, worthy of note that Cavendish did not himself interpret his experimental results as we interpret them to-day. He regarded 'dephlogisticated air' [oxygen] as 'nothing but dephlogisticated water, or water deprived of its phlogiston.' He said: 'We must allow . . . that inflammable air [hydrogen] is either pure phlogiston . . . or else water united to phlogiston' (*l.c.* pp. 187, 140).

The formation of water by burning H and O was thought of by Cavendish as the restoration of phlogiston to water that had been deprived of this principle. 'Water,' he said, 'consists of dephlogisticated air' united to 'phlogiston.' Cavendish evidently thought of H and O as what we might now call *forms of water*; one of these was water with too little phlogiston, and the other was water with too much phlogiston; the explosion restored the phlogistic balance, and the properties of water were apparent. When Lavoisier had interpreted Cavendish's results, Cavendish spoke of Lavoisier's explanation as an hypothesis: 'According to this hypothesis we must suppose that water consists of inflammable air united to dephlogisticated air' (*l.c.* p. 150). Cavendish established the fact that water is the product of burning a mixture of H and O in the ratio (approximately) of 2 vols. H to 1 vol. O; but he stated this fact, in language that no longer carries a definite meaning with it. Lavoisier added to the experimental basis whereon the fact rested, and he expressed the fact in language that still is clear, definite, and descriptive.

Formation.—1. By the direct union of H and O by igniting a mixture of these elements. 2. By deoxidising metallic oxides, and many other compounds that contain O, by heating with H.—3. By the decomposition of many compounds containing H and O, by heat, or by reactions with other substances.

According to Freyer a. V. Meyer (*B.* 25, 622), a mixture of H and O in the ratio 2H:O does not explode when slowly passed through a glass tube at 606°, and the temperature of ignition of the wet, gaseous mixture is between 650° and 730°. Askenasy a. V. Meyer (*A.* 269, 49) found that when pure, dry electrolytic gas was passed at a moderate rate through a glass tube heated to 518°, only 0.7 to 1.7 mgms. of water were produced in ten hours; and that a little more water, but still only a very small quantity, in proportion to the total quantity of H and O, was formed at 606°. Experiments made to determine the relation between the quantity of water formed and the time of the experiment showed that no constant relation could be arrived at, even when every precaution was taken to insure equality of conditions; the irregular action of the surfaces of the vessels was probably the cause of the irregularities in the results.

Davy (*T.* 1817) found that electrolytic gas did not explode when the pressure was so reduced

that the gas was rarefied to $\frac{1}{3}$ of its ordinary density. Thomas (*O. J.* 36, 215) found that the gas exploded at 168 mm. pressure. L. Meyer a. Seubert (*C. J.* 46, 586) found that the sparks from a Ruhmkorff coil caused the combination of c. $\frac{2}{3}$ of a quantity of electrolytic gas at c. 70 mm. pressure, and that the remainder combined when the pressure was increased until it became the same as before the first explosion; this result is in keeping with Bunsen's determinations of the quantity of oxygen needed to prevent the explosion of 2H + O (*v. M. a. S.* 7, c. p. 588). Dixon (*T.* 1884, 634) noticed that electrolytic gas did not explode at a pressure under 70 mm., but that explosion occurred under 75 mm. pressure (*cf. D.*, *l.c.* p. 642).

According to the experiments of Dixon (*l.c.*), 'the union of oxygen and hydrogen is not affected by the presence or absence of water'; dry electrolytic gas exploded by the spark at a pressure between 70 mm. and 75 mm., and the wet gas exploded at the same pressure.

The velocity of explosion of electrolytic gas was found by Berthelot and Vieille (*C. R.* 95, 151) to be 2,810 metres per second (*cf. Explosion*, vol. ii. p. 530).

Preparation.—Stas (*Chem. Propert.* 110) prepared pure water as follows. When large quantities were required, spring-water was *very slowly* distilled through a long copper tube, bent into zigzag form, completely filled with pure copper turnings that had been oxidised by strongly heating in O, the copper tube being surrounded by alumina and sand, and heated to full redness; the distillate was then distilled in a apparatus of platinum.

The second method recommended by Stas, especially when comparatively small quantities of pure water are required, is based upon destroying the organic matter in distilled water by the action of K manganate and permanganate. The process is described by Stas as follows:—

I prepared potassium manganate by reacting on manganese oxide with caustic potash and potassium chlorate. I shook up the powdered product with water, just sufficient to dissolve the manganate that had been formed, and allowed the mixture to settle in a closed vessel. I then added 4 or 5 p.c. of the clear, dark-green solution to the spring water which was to be distilled, and allowed the components of this mixture to react for 24 hours. I then poured into the distillation vessel one or two litres of the conc. solution of potassium manganate that had been mixed with an equal volume of conc. caustic potash solution; this solution of potash was sufficiently conc. to make the salt so stable that its dilute solution could be heated for a long time without decomposition. I then filled the distillation vessel to c. $\frac{2}{3}$ with the water which had been in contact with the potassium manganate, and distilled in the ordinary way. When boiling began I moderated the heat, in order to prevent the liquid, which frothed much for some minutes, from passing over. When the frothing had stopped, the water *slowly* be boiled rapidly without the least inconvenience. When $\frac{1}{2}$ of the water has distilled over, that which then distils is completely free from organic substances, and also from mineral substances, if the upper part of the distillation vessel is furnished with disphragms to hold back the extremely small drops that are always carried forward when a liquid is boiled vigorously.

Stas says that water thus prepared is perfectly free from organic matter. When he wished to obtain water absolutely free from any form of solid matter, Stas re-distilled the water that had been purified as described above, using as condenser a long tube of platinum soldered with gold. It is advisable to distil the water just before it is to be used.

On one occasion Stas used rain-water instead of well-water, and he found distinct quantities of ammonia in the distilled water thus prepared. To remove this he recommends to re-distil with the part of NaHSO_4 or KHSO_4 .

Composition of water.—The gravimetric composition of water was determined by Berzelius & Dulong (*A. Ch.* [2] 15, 86) and by Dumas (*A. Ch.* [8] 8, 189) by passing pure H over a weighed quantity of red-hot CuO , and weighing the water produced and the copper which remained. The results gave the ratio $\text{H}:\text{O} = 1:8$ (B. a. D.) and 1:7.98 (U.). An extended series of measurements by the same method, with many precautions, by Dittmar & Henderston (*C. N.* 67, 127, 139, 151, 164 [1898]) gave the ratio $\text{H}:\text{O} = 1:7.9827$.

Several measurements have been made of the proportion by volume in which H and O combine to form water. Gay-Lussac in 1805, and Humboldt in 1805 (*A. Ch.* 53, 239), found the volumetric ratio of $\text{H}:\text{O}$ to be 2:1. Morley, in 1891 (*Am. S.* [3] 41, 220, 276), determined the ratio of $\text{H}:\text{O}$ to be 2.00023:1 by directly measuring the volumes of the gases. In 1892 Leduc (*C. R.* 116, 1248) found the ratio $\text{H}:\text{O} = 2.0037:1$, from determinations of the relative densities of H, O, and electrolytic gas. In 1893 Scott (*T.* 184, 543) completed a most carefully performed series of syntheses of water by sparking mixtures of H and O, and determined the most probable value of the volumetric ratio $\text{H}:\text{O}$ to be 2.00245:1.

Properties.—Water is a clear, transparent, almost colourless, tasteless, odourless liquid. A column of water appears slightly blue when looked at lengthwise. Bunsen (*A.* 72, 44) pointed out that the slight blue colour of water may be observed by looking at a shining white object through a column of water 2 metres long, contained in a tube blackened inside. V. Meyer (*B.* 15, 297) recommends to join five wide, thin-walled glass tubes, c. 40 mm. internal diameter, and each c. 1½ metres long, by wide caoutchouc tubing, and thus to form a tube c. 7½ metres long; to lay the tube perfectly horizontal, and to close the end by smooth glass plates held in position by metallic clasps; then to cover the tube with black cloth. On looking through the tube the field of view appears quite colourless, but on now filling the tube with pure water (by means of brass tubes passing through the metallic clasps) a deep-blue colour is seen on looking through the column of water.

The boiling-point of water is 100° under the pressure of 760 mm. Zeuner (*Grundzüge der mechanischen Wärmetheorie*, Tab. 19 [1877]) gives the following table, showing the increase of boiling-point with increase of pressure:—

Pressure in atmos.	Boiling-point.	Pressure in atmos.	Boiling-point.
1 100		8 179.81	
2 120.6		9 176.77	
3 133.91		10 180.31	
4 144		11 184.60	
5 152.22		12 188.41	
6 159.22		13 192.08	
7 165.84		14 195.53	

An elaborate table is given by Broch (*Trav. et Mém. des Bureaux Internat. des Poids et Mes.*,

1, 46 [1891]) based on Regnault's determinations; the table gives the b.p. of water for each .1 mm. from 680 to 800 mm. pressure. (The table is given in Landolt & Börnstein's *Physikalisch-Chemische Tabellen* [Berlin, 1883], pp. 47–49.)

The melting-point of ice is slightly lowered by pressure. J. Thomson (*T. E.* 16) calculated that the m.p. would be lowered by $n \cdot 0075^\circ$ for an increase of n atmospheres; W. Thomson (*P. M.* [3] 37, 123) confirmed this calculation by determining the m.p. of ice at 8.1 and 16.8 atmos. Mousson (*A. Ch.* [3] 56, 252) kept water liquid, at -5° by greatly increasing pressure, and he found that at c. 13,000 atmos. pressure ice melted at -13° .

The specific gravity of water is greater at 4° than at any other temperature. Exner gives the temperature of maximum density as 3.946° (older determinations are tabulated by Exner, *W. A. B.* 68 (ii), 463 [1873]). The following table, showing the density and volume of water from 0° to 100° , is given by Volkmann (*W.* 14, 260 [1881]); it is based on the determinations of Hagen, Matthiessen, Pierre, Kopp, and Jolly:

Temp.	Density (in vacuo) i.e. wt. of 1 c.c. water in grams.	Volume of 1 gram water in c.c.
0	.999878	1.000122
1	.999933	1.000067
2	.999972	1.000028
3	.999993	1.000007
4	1.000000	1.000000
5	.999992	1.000008
6	.999969	1.000031
7	.999933	1.000067
8	.999882	1.000118
9	.999819	1.000181
10	.999739	1.000261
11	.999650	1.000350
12	.999544	1.000456
13	.999430	1.000570
14	.999297	1.000703
15	.999154	1.000847
16	.998904	1.000997
17	.998639	1.001162
18	.998363	1.001339
19	.998075	1.001527
20	.997772	1.001731
21	.997455	1.001939
22	.997124	1.002156
23	.996780	1.002383
24	.996423	1.002621
25	.996054	1.002868
30	.99577	1.00425
35	.99427	1.00586
40	.99236	1.00770
45	.99035	1.00974
50	.98817	1.01197
55	.98584	1.01436
60	.98334	1.01694
65	.98071	1.01967
70	.97789	1.02261
75	.97493	1.02572
80	.97190	1.02891
85	.96875	1.03225
90	.96549	1.03574
95	.96209	1.03941
100	.95855	1.04323

Rossetti (*P. Ergänzbd.* 5, 268 [1871]) gives the densities and volumes of water for each degree from -10° to 100° , referred both to water at 0° and to water at 4° as unity. The S.G. of ice is c. .916 at 0° (water at $0^{\circ}=1$); according to recent determinations by Zakrzewski (*W.* 47, 155 [1895]) the value is .916660.

The expansion of water for various intervals of temperature has been measured by various observers; putting $V_t = V_0 (1 + at + bt^2 + ct^3)$, the following values are given by Kopp (*P.* 72, 1 [1847]); cf. Pierre, *P.* 86, 451; Weidner, *P.* 123, 400; Matthiessen, *P. M.* [4] 31, 149; Rossetti, *P. Ergänzbd.* 5, 268; Hirn, *A. Ch.* [4] 10, 32):

Temp.	a
0° to 25°	-.000061045
25° to 50°	-.000065415
50° to 75°	-.00005916
75° to 100°	-.00008645

For the expansion of water above 100° v. Mendeleeff (*A.* 119, 1).

As water freezes it expands by $\frac{1}{11}$ of its volume; one volume of water at 0° becoming 1.09082 volumes of ice at 0° .¹⁰ It expands when heated at temperatures below 0° ; Zakrzewski (*W.* 47, 155) gives the co-efficient of expansion .000077 (v. also Brunner, *P.* 64, 116; Struve, *P.* 66, 298; Marchand, *J. pr.* 35, 254).

The compressibility of water is small. Röntgen & Schneider (*W.* 33, 644) give the absolute compressibility at 17.95° as .0000462 per atmosphere of pressure (v. also Ramsay & Young, *T.* 1892; and cf. Grassi, *A. Ch.* [3] 31, 437; and Rankine, *P. M.* [4] 1, 548; also Amaury & Descamps, *C. R.* 68, 1664; and Calvetet, *C. R.* 76, 77).

A table showing the volume of 1 kilo. of

saturated water vapour and the weight (in kilos.) of 1 c. metre of the vapour, at temperatures from 0° to 200° , is given by Zeuner (*v. Landolt & Börnstein's Physikalisch-chemische Tabellen* [Berlin, 1883], p. 53; cf. Dieterici, *W.* 38, 1). According to Dieterici (*l.c.*) water vapour saturated at 0° behaves like a perfect gas.

The vapour pressure of water varies from .0288 mm. at -19° to 20926.4 mm. at 230° ; for complete tables calculated from Regnault's determinations v. Landolt & Börnstein's *Physikalisch-chemische Tabellen* [Berlin, 1883] pp. 40-46 (the vapour pressure is given for each 1° from -19°

b	c
.0000077183	-.00000003734
.0000077587	-.000000035408
.0000031849	.0000000072848
.0000031892	.0000000024487

to 101° , and for each 1° from 101° to 230°). Ramsay & Young (*T.* 1892) give a table of the vapour pressures of water up to 270° . In connection with the vapour pressures of water and ice, v. R. & Y. (*T.* 1884, 470). For an expression representing the vapour pressure of water at any temperature up to 325° , v. Antoine (*C. R.* 113, 328).

The spec. heat of water increases as temperature rises; the quantity of heat required to raise 1 g. of water from t° to $t^{\circ}+1$ is taken as unity in determinations of the spec. heats of other substances. The following table presents the data for S.H. of water at intervals of 10° from 0° to 230° (the memoirs by the different observers are: Regnault, *Acad.* 21, 729, [1847]; Jamin & Amaury, *C. R.* 70, 661 [1870]; Bosscha, *P. Jubelbd.* 549 [1874]; von Münchhausen, *W.* 1,

t° (air therm.)	Regnault	Jamin & Amaury	Bosscha	v. Münchhausen	Henrichsen	Baumgartner
0°	1.0000	1.0000	1.0000	1.0000	1.0000	1.0000
10°	1.0005	1.0111	1.0022	1.0043	1.0036	1.0031
20	1.0012	1.0225	1.0044	1.0085	1.0079	1.0061
30	1.0020	1.0341	1.0066	1.0128	1.0131	1.0092
40	1.0030	1.0459	1.0088	1.0170	1.0191	1.0123
50	1.0042	1.0580	1.0110	1.0213	1.0259	1.0154
60	1.0056	1.0703	1.0132	1.0255	1.0335	1.0184
70	1.0072	1.0829	1.0154	1.0298	1.0419	1.0215
80	1.0090	1.0957	1.0176	1.0340	1.0511	1.0246
90	1.0109	1.1087	1.0198	1.0383	1.0612	1.0276
100	1.0130	1.1220	1.0220	1.0425	1.0720	1.0307
110	1.0155	1.1355	1.0242	1.0468	1.0837	1.0338
120	1.0177	1.1493	1.0264	1.0510	1.0961	1.0368
130	1.0204	1.1632	1.0286	1.0553	1.1094	1.0399
140	1.0232	1.1775	1.0308	1.0595	1.1235	1.0430
150	1.0262	1.1920	1.0330	1.0638	1.1384	1.0461
160	1.0294	1.2067	1.0352	1.0680	1.1540	1.0491
170	1.0328	1.2217	1.0374	1.0723	1.1706	1.0522
180	1.0364	1.2369	1.0396	1.0765	1.1879	1.0553
190	1.0401	1.2523	1.0418	1.0808	1.2060	1.0583
200	1.0440	1.2680	1.0440	1.0850	1.2249	1.0614
210	1.0481	1.2839	1.0462	1.0893	1.2447	1.0645
220	1.0524	1.3001	1.0484	1.0935	1.2652	1.0675
230	1.0568	1.3165	1.0506	1.0978	1.2866	1.0706

592; 10, 284 [1877 and 1880]; Henrichsen, W. 8, 83 [1879]; Baumgartner, W. 8, 648 [1879].

The following values for S.H. of water, from 0° to 85°, are given by Bartoli a. Stracciati (*A. Ch.* [6] 29, 285); the values in the column 'calculated' were obtained by using the formula:

$$\begin{aligned} \text{S.H.} &= 1.006630 \\ &- .000593962t \\ &+ .000004338650t^2 \\ &+ .000000425520t^3 \\ &- .000000002819t^4 \end{aligned}$$

The unit is the quantity of heat given out by 1 gram water at 15° in cooling, to 14°.

°	S.H. calcd.	S.H. observed.
0°	1.006630	1.00664
1	1.006641	1.00601
2	1.005463	1.00513
3	1.004898	1.00489
4	1.004350	1.00435
5	1.003820	1.00383
6	1.003307	1.00331
7	1.002824	1.00283
8	1.002362	1.00233
9	1.001927	1.00190
10	1.001522	1.00149
11	1.001146	1.00111
12	1.00080	1.00078
13	1.000496	1.00048
14	1.000224	1.00023
15	0.999990	1.00000
16	0.999795	0.99983
17	0.999642	0.99968
18	0.999530	0.99959
19	0.999462	0.99951
20	0.999439	0.99947
21	0.999463	0.99950
22	0.999533	0.99955
23	0.999652	0.99964
24	0.999821	0.99983
25	1.000040	1.00005
26	1.000311	1.00031
27	1.000633	1.00064
28	1.000967	1.00098
29	1.001438	1.00143
30	1.001921	1.00187
31	1.002459	1.00241
32	1.003054	—
33	1.003668	—
34	1.004409	—
35	1.005170	—

The S.H. of ice is considerably less than that of water. Regnault's determinations gave 47.4 between -75° and 0°; the determinations of Person a. Desains gave 50.4 between -20° and 0°; Ramsay a. Young (*T.* 1884, 475) give the value 5 as the mean of various experiments. S.H. of water gas at 100° is given by Strecker (*W.* 37, 85) as .37 referred to an equal weight of water = 1, and 1.36 referred to an equal volume of air = 1; the ratio $\frac{\text{S.H.p.}}{\text{S.H.v.}}$ given by S. is 1.4.

Jaeger (*W.* 36, 165 [1889]) gave the value 1.33 to this ratio, and Cohen (*W.* 37, 628 [1889]) gave the value 1.287 for the temperature interval 144° to 800°.

The heat of vaporisation of water—i.e. the quantity of heat required to convert 1 g. of water at 100° into steam at 100°—is 835.77

gram-units, according to Favre a. Silbermann (*A. Ch.* [3] 87, 461). The following values are given for the heat required to convert 1 g. of water at t° completely into water vapour; 606.5 when $t = 0^\circ$, 637 when $t = 100^\circ$, 676.6 when $t = 230^\circ$ (Regnault, *Acad.* 21, 635); Dieterici (*W.* 38, 1) gives 596.8 when $t = 0^\circ$; Regnault (*l.c.*) gives the formula $\lambda = A + Bt$ for the total heat of vaporisation of water at different temperatures, and gives the values $A = 606.5$, $B = .305$.

According to Sakhrat (*C. J.* 61, 495 [1892]), the temperature of the steam escaping from a boiling salt solution is exactly the same as that of the solution.

The heat of fusion of ice, i.e. the quantity of heat required to convert 1 g. of ice at t° into 1 g. of water at t° is given as follows by different observers (the values are in gram-units of heat): -79.24 and 79.06 when $t^\circ = 0^\circ$ (Regnault, *A. Ch.* [3] 8, 19); 79.25 when $t = 0^\circ$, 74.2 when $t = -10^\circ$, 80.22 when t varies from -2° to -21° (Person, *A. Ch.* [3] 21, 295; 30, 73); 77.85 at -2.8° , 76.75 at -4.995° , 76.11 at -6.28° , 76.0 at -6.6° (Pettersson, *J. pr.* [2] 24, 129).

The thermal conductivity of water, from 10° to 18°, was determined by Winkelmann (*P.* 153, 481) to be .154; Bottomley (*Pr.* 31, 300) obtained nearly the same value; this figure means that heat sufficient to raise .154 mgm. water from 0° to 1° passes per second through a layer of water 1 mm. thick and 1 sq. mm. area, when the difference between the temperatures of the two surfaces of the layer is maintained at 1°. For electrical conductivity of water *v. Reactions*, No. 2.

The refractive indices of water at different temperatures, and for different lights of determinate wave-lengths, have been measured by many observers. The following values have been found for μ_D : 1.33120 at 19.9°, 1.33051 at 23.7°, 1.33050 at 26° (Brühl, *B.* 24, 644). For detailed tabulation of the results obtained by Fraunhofer, van der Willigen, Baillé, Damien, Landolt, Wüllner, and Rühlmann, *v. Landolt a. Börnstein's Physikalisch-Chemische Tabellen* [Berlin, 1883] 205; *cf.* also Perkin (*C. J.* 61, 293), who gives values for μ for the lines A C D and F, at 15° and 83.7°.

Observations have been made on the absorption spectrum of water and water-gas, but the matter has not been thoroughly investigated (*v. Vogel*, *P.* 156, 326; Jansen, *B.* A. 1866, 11).

Water crystallises, as ice, in rhombohedral forms; snow is generally found crystallised in six-sided stars derived from six-sided prisms.

Molecular weight of liquid water. Several observations have been made which tend to show that the molecular weight of liquid water is greater than 18. Paterno (*B.* 21, 3180), from measurements of the lowering of the freezing-point of water dissolved in acetic acid, concluded that the mol. w. might be 19, or might perhaps be 36. From the depression of the freezing-point of paratoluidine by water dissolved therein, Eykman (*Z. P. C.* 4, 510) concluded that the mol. w. of liquid water is probably 36, and this conclusion was strengthened by Walker's experiments on the connection between heats of fusion and solubility (*Z. P. C.* 5, 194). From measurements of the surface tension of water Ramsay and Shields (*C. J.* 68, 1069 [1893]) con-

clude that the mol. w. of liquid water is probably 72 at the ordinary temperature.

Reactions.—1. In 1847 Grove (*T.* 1847. 1) showed that water was decomposed into H and O by heat. Grove formed a little ball on the end of a Pt wire, by fusing the Pt, heated the globe of Pt to whiteness by an electric current, and plunged it into a little air-free water, nearly boiling, in a small basin, with a test tube full of air-free water arranged to collect any gas that might come off. Deville (*C. R.* 56, 195, 322 [1863]) found that H and O were given off in considerable quantities when molten Pt was plunged under water. D. noticed no decomposition when steam was passed through a Pt tube heated to bright redness, but by passing a current of an indifferent gas, such as CO, through the hot tube, and thus sweeping away the products of decomposition, H and O were obtained.—2. Water is scarcely decomposed by an electric current. Kohlrausch found the electrical conductivity of the purest water he could obtain by distillation *in vacuo* to be 2.5×10^{-8} in C.G.S. units, or c. 72 billionths of the conductivity of Hg (*P. M.* [5] 18, 542). By calculations based on this result, Ostwald concluded that in a litre of pure water the weight of water dissociated into H and OH ions, expressed in gram-molecules, is 6×10^{-8} (*Z. F. C.* 11, 521). By other methods of calculation, based on other data, Ostwald arrived at the value 2 to 9×10^{-8} for what has been called the *dissociation constant* of water (*Z. P. C.* 11, 521); Wijs, by calculations based on the hydrolysis of methyl acetate, obtained the values 1×10^{-7} (*Z. P. C.* 11, 492), and 14×10^{-8} (*ibid.* 12, 514); Arrhenius obtained the value 1125×10^{-8} (*ibid.* 11, 827); and Bredig, the value 6×10^{-8} (*ibid.* 11, 829). Later experiments on the conductivity of water by Kohlrausch and Heydweiller (*Z. P. C.* 14, 916 [1894]) with water that had been distilled *in vacuo* ten years ago, had then stood in a vessel filled with water, and been again distilled *in vacuo*, gave the following results:—conductivity ($Hg = 1$) .014 at 0°, .04 at 18°, .058 at 25°, .089 at 34°, .176; all these to be multiplied by 10^{-10} . K. a. H. say that 1 mm. of this water at 0° had a resistance = that of 40 million kilometres of Cu wire of the same area. K. a. H. calculate that in 1 litre of the purest water at 18° there is .00008 mgm. H as free ions, and .000105 mgm. at 25°.—3. Steam is decomposed by electric sparks; for condition and details of results v. Thomson (*Pr.* 53, 90).

The reactions of water are so many that an approximate classification of them into groups is all that can be attempted here.—4. Many metals react with water, at temperatures varying from the ordinary to a full red heat, forming oxides or hydroxides and giving off H. The following metals decompose cold water: Ba, Ca, (Ce?), (La?), Li, K, Rb, Na, Sr. Al, Fe, Pb, Mg, (Mn), Mo, Si react at c. 100°; and most of the other metals at temperatures from c. 100° to a full red heat.—5. Many non-metals react, generally slowly, with water, forming acids and giving off O. F rapidly decomposes water at the ordinary temperature; Cl reacts slowly at the ordinary temperature, and somewhat more rapidly at a red heat; Br reacts more slowly than Cl; I has probably a very slight (any) action. S and P react slowly at 100°; Se is said not to

decompose water at 160°. Carbon gives off H at a red heat. Boron acts like a metal, giving off H at a red heat.—6. Many haloid compounds react with water, giving oxyhaloid compounds or oxides, and haloid acids.—7. Some metallic sulphides react with steam to form oxides and H₂S. 8. A few of the lower oxides decompose water; e.g. CrO₂·xH₂O at the ordinary temperature, and CO at c. 600°.—9. Water reacts with many oxides to form hydroxides which are either basic or acidic; in some cases hydrates are formed. Hydrates of various salts are also produced by combining the salts with water (v. HYDRATES, vol. ii. p. 703; cf. HYDROXIDES, vol. ii. p. 733).—10. Water dissolves very many compounds of the most different properties (v. SOLUTIONS, vol. ix. p. 484).

Small quantities of water often bring about chemical changes that do not occur when the substances are perfectly dry; for instance, a mixture of dry CO and O is not exploded by sparks, but a trace of water suffices to start the change (v. Baker, *C. J.* 65, 611 [1894]).

The acidic and basic characters of water are so nearly balanced that the compound cannot be classed among either acids or basic bodies. The chemical relations of water to the compounds formed by reactions between it and other substances are determined chiefly by the chemical characters of the substances that react with it; thus the relations of HOH to M₂(OH)₂, formed by the interaction of water and metals, are those of an acid to its salts, whereas the relations of HOH to HX, formed by the interactions of water and non-metals, are those of a basic hydroxide to salts derived therefrom. The relations between both classes of derivatives of water and the parent compound are sometimes expressed by saying that the compounds belong to the *water type* (v. TYPES, vol. iv. p. 811). M. M. P. M.

WAX. A term applied to various natural solids more or less resembling bees'-wax. They are compound ethers, but differ from fats in yielding monovalent alcohols and not glycerin on saponification. They melt below 100°, are insol. water, sl. sol. or insol. alcohol, and sol. ether. They are not volatile.

Bees'-wax. [64°]. S.G. .965. Consists of a portion (about 5 p.c.) soluble in alcohol (cerin) and a portion insoluble in alcohol (myricin). Myricin is myricyl palmitate (Brodie, *A.* 67, 180; 71, 144). Cerin is chiefly composed of cerotic acid C₂₆H₅₂O₂ [90°], and an acid melting at 78° (Schalfejeff, *B.* 9, 278, 1688; Nafziger, *A.* 224, 246). There is also present one or more acids whose lead salts dissolve in ether and whose Ba salts dissolve in alcohol, and which therefore probably belong to the oleic series. Myricin may be saponified by alcoholic potash, and the myricyl alcohol separated from potassium palmitate by extraction with ligroin. Crude myricin yields CCl₄ and C₂Cl₄ when heated with I and excess of SbCl₅ at 400° (Hartmann, *B.* 24, 1022). Bees'-wax containing two hydrocarbons, one of which [60°] (c. 275° at 11 mm.) is probably *n*-heptaicosane C₂₇H₅₆, and the other [68°] (c. 340° at 11 mm.) *n*-hentriacontane C₃₁H₆₂ (Schwalb, *A.* 235, 106). According to Schwalb, the myricyl alcohol of bees'-wax has the formula C₃₁H₆₂O [85°], and is converted by heating with

soda-lime into an acid $C_{11}H_{19}O_2$ [89°], which forms a methyl ether [71°] and an ethyl ether [70°]. Among the products of saponification of bees'-wax, ceryl alcohol $C_{27}H_{54}O$ or $C_{28}H_{56}O$, and an alcohol $C_{26}H_{52}O$ or $C_{27}H_{54}O$ occur. The last-mentioned alcohol when heated with soda-lime gives an acid $C_{26}H_{50}O_2$ or $C_{27}H_{52}O_2$ [75.5°].

Carnauba wax v. vol. i. p. 710.

Chinese wax, which is produced by an insect, is almost entirely composed of ceryl cerotate ($C_{27}H_{54}O_2$) ($C_{27}H_{54}O_2$, (Brodie, A. 67, 199).

Cork wax v. CORK.

Pine wax v. CROTOPIC ACID.

Sugar-cane wax v. CEROSEIN.

Japan wax. [42°-55°]. Obtained in the East from *Rhus succedanea*. It appears to be really a fat, since palmitin is its chief component. It also contains the ether of a fatty acid of higher melting-point than stearic acid (Sthamer, A. 43, 343; Buri, Ar. Ph. [3] 14, 403).

Wax of Ficus gumiflua of Java contains an alcohol $C_{11}H_{22}O$ [73°], v. sol. ether, and a small quantity (5 p.c.) of isoceryl alcohol $C_{27}H_{54}O$, sl. sol. ether (Kessel, B. 11, 2112).

Myrtle wax. [49°]. Got by boiling the berries of *Myrica cerifera* of North America with water (Moore, J. 1862, 500). Consists of palmitic and some lauric acid and (20 p.c.) of palmitin.

Opium wax. Contains ceryl cerotate and ceryl palmitate (Hesse, B. 3, 637).

Tobacco wax. Contains $C_{26}H_{52}O_2$ [63°], insol. cold alcohol, sol. ether and a small quantity of $C_{26}H_{52}O_2$ [64.5°], nl. sol. cold ether (Kissling, B. 16, 2433).

Coca leaf wax (Hesse, A. 271, 214). The wax from Trujillo coca is palmityl-(β)-amyirin $C_{26}H_{52}O_2$ [75°] $[\alpha]_D = 54.5^\circ$. On saponification it yields palmitic acid and (β)-amyirin $C_{26}H_{52}O$ [196°] $[\alpha]_D = 94.2^\circ$, which yields an acetyl derivative [236°] and a benzoyl derivative [228°]. The wax from the broad-leaved coca of Peru and Bolivia melts at 70°; contains palmityl-(β)-amyirin and a ketone, (β)-cerothinone $C_{26}H_{50}O$ [66°], m. sol. alcohol, ether, and ligroin. The wax from Java coca contains the same substances, and also some ceryl cerotate and ethers of myristic acid and of oyceroic acid $C_{27}H_{54}O_2$ [82°], which is v. e. sol. hot alcohol and ligroin, v. sl. sol. ether, and is converted by Ac_2O at 100° into cerotic acid $C_{26}H_{52}O_2$ [70°].

WHEY-PROTEID v. MILK.

WINE OIL. Light oil of wine. An oil-obtained in the preparation of ether by distilling alcohol with H_2SO_4 . The ether is shaken with milk of lime and fractionally distilled, the successive fractions being ether, alcohol, and wet alcohol. Light oil of wine (25 to 3 p.c. of the alcohol etherified) rises to the surface when the last fraction (90°-120°) is allowed to stand. When dried over $CaCl_2$ it has S.G. 0.903. It contains $C_{11}H_{22}$ (157), $EtOC_2H_5$ (112),

$Et.CO.O.C_2H_5$ (154°), and $CH_3.CO.C_2H_5$ (164°) (Hartwig, J. pr. [2] 23, 449).

Heavy oil of wine, which passes over when the temperature is raised after the preparation of ether, consists of $Et.SO_4$ mixed with olefines (Claesson, J. pr. [2] 19, 259; Serullas, J. Ch. [2] 89, 152).

WINTERGREEN OIL contains methyl o-oxymethylene.

WINTERENE $C_{10}H_{18}$. (260°-265°). S.G. 0.934. $[\alpha]_D 11.2^\circ$ at 16°. A dextrorotatory sesquiterpene obtained by distilling winterbark (from *Drymis Winter-Forster*) with water (Arata a. Canzoneri, G. 18, 527). Coloured green by Br in $CHCl_3$.

WOOD v. LIGNONE.

WOOD GUM v. XYLEN.

WOOD NAPHTHA v. METHYL ALCOHOL.

WOOD OIL. *Gurjun Balsam*. Flows from incisions in the stem of *Dipterocarpus costatus*. It contains an essential oil, which gives a splendid violet colour when its solution in CS_2 (20 pts.) is treated with a drop of a cold mixture of HNO_3 and H_2SO_4 . The same reaction is exhibited by the balsam itself, and also, in a more transient manner, by cod-liver oil and copaiba balsam (Flückiger, Ph. [3] 7, 2). The essential oil consists chiefly of a terpene (255°) (Werner, J. 1862, 461), which composes 65 p.c. of the balsam (Guibourt, J. 1876, 907). The resin contains a neutral substance, $C_{26}H_{50}O_2$, which crystallises from light petroleum in triclinic prisms [120°-130°]; it dissolves in conc. H_2SO_4 , and is reprecipitated from the resulting reddish solution by adding water. It is not affected by potash-fusion (Flückiger, Ar. Ph. [3] 12, 58). A substance $C_{26}H_{50}O_2$ [129°] is described by *Buxton* (M. 2, 516) as prod. by adding water to an alcoholic extract of wood oil. It is neutral and insol. alkalis, and yields a diacetyl derivative (75°). It is perhaps identical with the compound $C_{26}H_{50}O_2$. Wood oil also contains gurjunic acid $C_{26}H_{50}O_2$ [220°], which crystallises from alcohol, distils with decomposition at 260°, and forms Ag_2A' .

WOOD SPIRIT v. METHYL ALCOHOL.

WORMSEED OIL. *Oleum Cinsae*. Obtained by steam-distillation from wormseed, the flower-buds of *Artemisia Vahlana*, A. Sieber, and *A. incalla* (Trommsdorff, Tr. N. J. 8, 812; Völckel, A. 38, 110; 87, 312; Hirzel, J. 1854, 591; 1855, 655; Kraut a. Wahlforss, A. 128, 293; Faust a. Homoyer, B. 7, 1429; Hell a. Ritter, B. 17, 2609; Wallach a. Brass, A. 225, 291). It consists chiefly of cineol $C_{15}H_{26}O$. Wormseed (*A. Gallica*) also contains betaine and choline (Jahns, B. 26, 1493).

WRIGHTINE $C_{11}H_{19}N$. [122°]. Occurs in the juice of *Wrightia antidysenterica* (Stenhouse, Ph. [2] 5, 493; Warnecke, B. 10, 60). Needs with bitter taste, sl. sol. water, v. sol. alcohol and ether. Conc. H_2SO_4 , at 100° gives a dark green colour, turned dark blue by adding water. Wrightine, is probably identical with conessine (q. v.).

X

XANTHALINE $C_8H_6N_2O_2$. [506°]. Occurs in opium (T. a. H. Smith, *Ph.* [8] 23, 798). White crystalline powder, insol. water and alkalis, sl. sol. hot alcohol, m. sol. benzene, v. e. sol. chloroform. Weak base, forming yellow salts from which it is, ppd. by hot water. Conc. H_2SO_4 forms a deep-orange solution, from which water ppts. the sulphate as yellow needles. Hot HNO_3 does not decompose it. Zinc and H_2SO_4 reduce it to hydroxanthaline $C_8H_8N_2O_2$, which forms white crystals [137°], nearly insol. water, v. sol. alcohol and benzene, and forms easily soluble crystalline salts. Hydroxanthaline is coloured deep-violet by H_2SO_4 (even free from HNO_3), the colour being destroyed by water, but reproduced by H_2SO_4 .— $B^+H_2Cl_4$ aq.: yellow needles. Gives off all its acid at 156°.

XANTHAMIDE v. *Ethyl ether of (β)-Thio-carbamic acid*.

XANTHATES. The salts $RS.CS.OEt$ where R is a metal; v. *ETHYL DITHIOCARBONATE*.

XANTHIC ACID v. *ETHYL DITHIOCARBONATE*.

XANTHINE $C_8H_6N_4O_2$, i.e.

$NH_2CH:C(NH)CO$. *Xanthic oxide*. Mol. w. 152. S. 007 in the cold; 08 at 100°. Occasionally found in urinary calculi (Marcel, *Essay on Calculi*, London, 1819; Liebig a. Wöhler, A. 26, 840; Lebon, C. R. 73, 47) and in urinary deposits (Bence Jones, C. J. 15, 78). Occurs in small quantity in the urine of man, in the pancreas, spleen, and liver of oxen, in the thymus gland of the calf, in muscle of mammals and fishes (Scherer, A. 107, 314; 112, 257; Städeler, A. 111, 28; 116, 102; Dürr, A. 184, 45; Kossel, H. 6, 422), in some kinds of guano (Unger a. Phipson, C. N. 6, 16), and in yeast (Schindler, H. 18, 432). Occurs also in lupin seeds (Salomon, J. 1881, 1012; Schulze a. Barbieri, J. pr. [2] 27, 358), in pumpkin-seeds (E. Schulze, J. pr. [2] 32, 457), and in tea (Baginsky, H. 8, 396).

Formation.—1. By the action of nitrous acid on guanine (Strecker, A. 108, 141; 118, 151; 121, 121; Balke, J. pr. [2] 47, 542).—2. In small quantity by heating a mixture of $HOAc$ and aqueous HCl (Gautier, Bl. [2] 42, 141).

Preparations.—1. Separates as a crystalline powder when $NaNO_2$ (8 g.) is added slowly to a solution of guanine (10 g.) in H_2SO_4 (20 g.) and water (150 g.) at 75° (Fischer, A. 215, 309).—2. The aqueous extract of sprouting lupin seeds is evaporated, the residue treated with alcohol, and the alcoholic filtrate evaporated. The residue is dissolved in water, and $AgNO_3$ and NH_3 added. The gelatinous pp. is dissolved in hot HNO_3 (S.G. 1.1), which yields on cooling a crystalline compound of hypoxanthine and silver nitrate, and on adding NH_3 to the filtrate silver-xanthine is ppd. (S. a. B.).—3. Urine is ppd. with baryta-water; the filtrate is evaporated to a small bulk and boiled with cupric acetate. The pp. is dissolved in warm nitric acid and ppd. with $AgNO_3$; the pp. is crystallised from hot diluted HNO_3 , treated with ammoniacal $AgNO_3$, decomposed by H_2S , and the solution

evaporated.—4. A solution containing xanthine is treated with Fehling's solution and hydroxylamine hydrochloride, and the ppd. copper compound decomposed by H_2S . The xanthine may be further purified by preparing its lead salt and decomposing this with H_2S (Balke, J. pr. [2] 47, 552).

Properties.—Small scales (by evaporation) or powder composed of minute globules, nearly insol. cold water, insol. alcohol and ether. V. e. sol. KOH aq. and reppd. by CO_2 and other acids. Weak base. Does not form an acetate. A cold saturated aqueous solution of xanthine gives white pps. with $HgCl_2$ and $AgNO_3$, and a yellowish-green, flocculent pp. with hot cupric acetate. An ammoniacal solution of xanthine is ppd. by $HgCl_2$, $ZnCl_2$, $CdCl_2$, and $AgNO_3$. Xanthine reduces ammoniacal cupric chloride (Drechsel, B. 25, 2454). Xanthine evaporated with nitric acid leaves a yellow residue turned orange by KOH (but not by NH_3), the colour becoming violet-red on warming. Solid xanthine added to a mixture of bleaching-powder and $NaOH$ aq. on a watch-glass forms a dark-green spot, changing to brown and finally disappearing. Xanthine warmed with chlorine-water and a trace of HNO_3 , as long as gases escape, and then evaporated to dryness, yields a residue which is coloured rose-red by gaseous NH_3 (Weidel, A. 158, 365; Kossel, H. 6, 426).

Reactions.—1. Decomposed above 150°, giving off HCl , NH_3 , cyanogen, and CO_2 .—2. $KClO_4$ and HCl aq. at 60° form urea and alloxan.—3. Conc. HCl aq. at 230° forms glycocoll, formic acid, NH_3 , and CO_2 (E. Schmidt, A. 217, 311).—4. $NaOH$ (2 mols.) and $Pb(OAc)_2$ form a lead salt which, if dried and heated with MeI at 130°, yields theobromine (Fischer).—5. Slowly attacked by pure HNO_3 , the gas evolved consisting of nitrogen (1 vol.), CO_2 (4 vols.), and N_2O (11 vols.) (Franchimont, R. T. C. 6, 223).

Salts.— B^+HCl . Nodular groups of silky needles.— $B^+H_2SO_4$ aq. Scales, decomposed by water.— $B^+BaH_2O_2$. Sl. sol. water.— $B^+Cu_2O_2$. Formed by the action of Fehling's solution and hydroxylamine hydrochloride (Balke).— B^+AgO . Yellowish-white flocculent pp., got by adding $AgNO_3$ to an ammoniacal solution of xanthine. Blackens on boiling.— $NaC_8H_6N_4O_2$ aq. Minute needles.

Bromo-xanthine $C_8H_5BrN_4O_2$. Formed by heating xanthine with bromine at 100°, and also by the action of nitrous acid on bromoguanine (Fischer a. Reese, A. 221, 348). Crystalline powder, sol. conc. HCl aq. and H_2SO_4 , but reppd. by water; sl. sol. hot water and hot alcohol; sol. alkalis.

Isoxanthine $C_8H_6N_4O_2$, i.e.

$NH.CO.C(NH)CO.NH_2.CCH \gg N$. Formed by reducing diazo-isopitosomethyl-uracil $C_8H_6N_4O_2$ with $SnCl_4$ and HCl aq. (Behrend, A. 245, 223). Needles (containing jag); sl. sol. hot water. Dissolves in Ac_2O without change. On evaporation with HNO_3 , it leaves a residue coloured orange by

KOHAq. Yields $C_8H_7BrN_3O_2$ as, crystallising from water in six-sided tables.

Pseudo-xanthine $C_8H_7N_3O_2$. A product of the action of H_2SO_4 (2 pts.) on uric acid (1 pt.) at 120° (Schultzen a. Filehne, *B.* 1, 150). Formed also by the action of nitrous acid on adenine (Kossel, *H.* 10, 258). Powder, sl. sol. water; HClAq, and NH_4 Aq, v. sol. KOHAq. Its aqueous solution is acid in reaction, and on evaporation with HNO_3 leaves a lemon-yellow residue, which is turned orange on warming with KOHAq.

The name pseudo-xanthine is also given by Gantier (*Bl.* [2] 48, 19) to a substance $C_8H_7N_3O_2$ occurring in muscular tissue. This is a yellow powder, which forms a very soluble hydrochloride. Its aqueous solution is ppd. by $HgCl_2$, $AgNO_3$, and ammoniacal $Pb(OAc)_2$, but not by $Pb(OAc)_2$. This pseudo-xanthine also gives an orange colour when the residue, after evaporation with HNO_3 , is treated with potash.

Paraxanthine $C_8H_7N_3O_2$ [c. 284°]. Occurs in human urine (Salomon, *B.* 16, 195; 18, 3406; *H.* 13, 187; Thudichum, *H.* 11, 415; Kossel, *H.* 13, 302). Silky needles or monoclinic tables, insol. alcohol and ether, sl. sol. cold water, v. sol. hot water. Sol. NH_4 Aq and HClAq. Poisonous, acting like caffeine and theobromine. $AgNO_3$ added to its solution in HNO_3 or NH_4 Aq gives a gelatinous or flocculent pp. Picric acid forms a yellow crystalline pp. when added to its solution in HClAq. Gives a red colour (like xanthine) when the residue after evaporation with chlorine-water is exposed to gaseous NH_3 . Does not give an orange colour when KOHAq is added to the residue after evaporation with HNO_3 . Conc. NaOHAq forms a crystalline salt. KOHAq does the same. A solution of paraxanthine is ppd. by $Cu(OAc)_2$, phosphotungstic acid, $HgCl_2$, and ammoniacal lead subacetate, but not by mercuric nitrate.

Heteroxanthine $C_8H_7N_3O_2$. Occurs in urine of men and dogs (Salomon, *B.* 18, 3407; *H.* 11, 412). Amorphous powder, v. sl. sol. cold water, sol. NH_4 Aq, insol. alcohol and ether. Its solution in HClAq is not ppd. by picric acid. $AgNO_3$, $HgCl_2$, $Cu(OAc)_2$, and ammoniacal lead subacetate give pps. When evaporated with chlorine-water and HNO_3 it leaves a residue which is coloured red by gaseous NH_3 , the colour changing to blue on addition of NaOHAq. NaOHAq forms a salt crystallising in tables, v. sol. water, sl. sol. NaOHAq. The hydrochloride forms sparingly soluble crystalline aggregates, which lose HCl on treatment with water.

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XANTHININE $C_8H_7N_3O_2$. S. 0025 in the cold; 0.25 at 100° . Formed by heating ammonium thionurate at 200° (Finck, *A.* 132, 298). Get also by heating pseudo-uric acid with H_2SO_4 to 150° (Grimaux, *Bl.* [2] 81, 535). White powder, nearly insol. water, sol. NH_4 Aq, forming a solution with blue fluorescence. Its solution gives a white pp. with $HgCl_2$ and a yellow pp. with $AgNO_3$. Not attacked by HNO_3 . Sol. KOHAq and reppd. by CO_2 . Sol. conc. H_2SO_4 , forming a laminar sulphate, decomposed by water with separation of xanthine. —E'Aq. O. Bulky yellow pp. got by pouring an ammoniacal solution of xanthine into excess of aqueous $AgNO_3$.

XANTHOCHELIDONIC ACID v. CHELIDONIC ACID.

XANTHOCERATININE v. CERATININE and LEUCOCERATININE.

XANTHOGALLOL $C_{12}H_7Br_3O_2$, *tc.*

$C_6H_4Br_2O \begin{smallmatrix} \diagup OCHBr_2 \\ \diagdown OCHBr_2 \end{smallmatrix} O$ (?). [122°]. Formed by adding pyrogallol (1 pt.) to bromine (10 pts.), leaving the mixture to stand for two hours, and then shaking with water and heating (Stenhouse a. Groves, *C. J.* 23, 1; *A.* 177, 191; 179, 287; Theurer, *A.* 245, 334). Tri-bromo-pyrogallol is an intermediate body in its preparation. Yellow laminae (from CS_2 and ligroin), v. sol. ether and CS_2 , m. sol. ligroin. Decomposed by boiling with water or alcohol. Very stable towards oxidising agents, even crystallising unaltered from conc. HNO_3 . Not reduced by sodium-amalgam or by zinc and dilute H_2SO_4 . Aniline in HOAc yields an anilide [205°], to which Theurer assigns the impossible formula $C_{12}H_7Br_3(NHPh)_2O$. *p*-Toluidine forms a corresponding *p*-toluide. Reacts with phenyl-hydrazine acetate.

Reactions. —1. NaOHAq forms hexa-bromobenzene dihydride $C_6H_2Br_6$ [199°], sl. sol. alcohol, which crystallises in prisms, while the mother-liquor contains a sodium salt of an acid $C_6H_2Br_6O_2$ [124°], which forms BaA'', crystallising from dilute alcohol in large white plates (Theurer). By the action of dilute NaOHAq on xanthogallol, Hantzsch a. Schmitter (*B.* 30, 2033) obtained $C_{12}H_7Br_3(OH)_2O_2$, which yields $Ba_2(C_{12}H_7Br_3O_2)_2$, and crystalline $C_{12}H_7Br_3AcO_2$. 2. Na_2CO_3 Aq converts xanthogallol in the cold into $C_{12}H_7Br_3O_2$, crystallising from benzene in needles [72°] and prisms [131°], yielding the crystalline derivatives $C_{12}H_7Br_3O_2NPhH$ and $C_{12}H_7Br_3O_2NHC_2H_5Me$. —3. HBr passed into a cooled solution of xanthogallol in MeOH forms $C_{12}H_7Br_3O_2(OMe)_2$, crystallising from MeOH in prisms [113°], and converted by boiling dilute NaOHAq into an acid $C_{12}H_7Br_3O_2(OMe)$, [105°], and by MeOH and hydrochloric acid into $C_{12}H_7Br_3Cl(OMe)$, [77°]. The brominated acid $C_{12}H_7Br_3O_2(OMe)$, reacts with aniline, forming crystalline $C_{12}H_7Br_3O_2(OMe)NHPh$. Conc. H_2SO_4 converts $C_{12}H_7Br_3O_2(OMe)$ into $C_{12}H_7Br_3O_2$, [65°]. —4. Hydrochloric acid gas passed into a cooled solution of xanthogallol in MeOH forms $C_{12}H_7Br_3Cl_2O_2(OMe)$, [86°], which is insol. water, v. sol. alcohol, does not react with aniline, and is decomposed by dilute alkalis. —5. HCl passed into an alcoholic solution of xanthogallol forms $C_{12}H_7Br_3Cl_2O_2(OEt)_2$, crystallising from alcohol in colourless prisms [75°], converted by NaOHAq into a product [92°]. $C_{12}H_7Br_3Cl_2O_2$ [104°] is a bye-product in the action of alcohol and HCl on xanthogallol. It forms large yellow crystals, v. sol. alcohol.

XANTHOGENIC ACID v. ETHYL DITHIOCARBONATE.

XANTHOMETHYLIC ACID v. METHYL THIOCARBONATES.

XANTHON is DIPHTERINIC KETONE OXIDE. XANTHOPURPURIN is *m*,*Di*-OXY-ANTHRAQUINONE.

XANTHOQUINIC ACID v. OXY-QUINOLINIC CARBOXYLIC ACID.

XANTHOREAMNIN $C_{12}H_7O_2$ (?). Obtained from Persian berries (the fruit of *Rhamnus infectoria*) by extracting with three times their

Properties.—Liquid. Not attacked by dilute HNO₃. Conc. HNO₃ on warming forms tri-nitro-xylene [176°], sl. sol. alcohol.

Reactions.—1. Oxidised by chromic acid mixture to isophthalic acid.—2. PCl₅ at 200° forms a hexachloride (Colson a. Gautier, *Bl.* [2] 45, 568).—3. Bromine in the dark forms C₈H₇Me.Br [1:3:4], while in direct sunshine C₈H₇Me.(CH₂Br) and C₈H₇(CH₂Br)₂ are produced (Schramm, *B.* 18, 1277; *M.* 8, 305).—4. AlCl₃ and gaseous HCl at 100° form benzene, mesitylene, and some *p*-xylene and *ψ*-cumene (Heise a. Töhl, *A.* 270, 168). On boiling with AlCl₃ the products are benzene, toluene, a little *p*-xylene, *ψ*-cumene, mesitylene, and durene (Anschütz, *A.* 235, 182).—5. On heating with MeI and I at 250° it yields *ψ*-cumene, mesitylene, and C₈H₁₄ (Payman a. Preis, *A.* 223, 320).—6. Ethyl-malonyl chloride at 60° in presence of AlCl₃ forms the ketone C₁₂H₁₄O₂ [63°] (Béhal a. Auger, *Bl.* [3] 3, 122).—7. Benzoyl peroxide forms dixylylene C₁₆H₁₄, S.G. 21.9984 (Lippmann, *M.* 7, 528).—8. CrO₂Cl₂ added to its solution in CS₂, ppts. chocolate brown C₈H₇Me.2CrO₂Cl₂, which is converted by water into *m*-toluic aldehyde and at 200° yields C₈H₇Me.CH(CrO₂Cl)₂ (Étard, *A. Ch.* [5] 22, 244).—9. CH₂Cl₂ and AlCl₃ form tetramethyl-anthracene [163°] (Friedel a. Crafts, *A. Ch.* [6] 11, 268).—10. PH₃I forms C₈H₁₄, on heating (Baeyer, *Z.* [2] 3, 455). HIAq and P at 280° form *m*-xylene hexahydride.

***p*-Xylene** C₈H₆Me₂ [1:4]. [13°] (Reissert, *B.* 23, 2242); [15°] (Jannasch). (138°). S.G. 3.8801 (K); ρ_{20}^4 860 (Gladstone, *C. J.* 59, 290). C.E. (0°–10°) 0.0098 (Pinette, *A.* 243, 51). μ_n 1.4854. μ_n 1.5253. S.V. 140 (Schiff). H.G. 1,084,274 (Stohmann, *J. pr.* [2] 35, 41). M.M. 12.79 at 20°–30° (Schönrock, *Z. P. C.* 11, 753). Critical temperature 344°. Occurs in coal-tar (*v. supra*) and in Galician petroleum (Pawlewski, *B.* 18, 1915). Formed by the action of MeI and sodium on *p*-bromo-toluene (Fittig, *A.* 136, 303; Jannasch, *A.* 171, 79) and on *p*-di-bromo-benzene (V. Meyer, *B.* 3, 753). Monoclinic prisms; $\alpha:b:c=2:32:1.2:34$; $\beta=69.5^\circ$ (Baeyer, *A.* 245, 141).

Reactions.—1. Dilute HNO₃ forms *p*-toluic acid.—2. Chromic acid mixture yields terephthalic acid.—3. PCl₅ at 190° gives C₈H₄(CH₂Cl)₂, and at 200° C₈H₄(CCl₂)₂ (Colson a. Gautier, *Bl.* [2] 45, 5, 507).—4. Bromine in the dark forms C₈H₇Br.Me, while in direct sunshine the products are C₈H₇Me.CH₂Br and C₈H₇(CH₂Br)₂ (Schramm, *B.* 18, 1276).—5. AlCl₃ and HCl at 100° act in the same way as with *o*-xylene.

References.—Bromo-, Bromo-nitro-, Chloro-, Dichloro-nitro-, Di-iodo-, Nitro-, and Oxy-xylenes.

XYLENE-AZO- compounds v. Azo- compounds.

XYLENE CARBOXYLIC ACID v. DI-METHYLBENZOIC ACID AND MESITYLENIC ACID.

***m*-XYLENE DICARBOXYLIC ACID** C₈H₆O₄, *i.e.* C₈H₄Me₂(CO₂H)₂ [1:3:4:5]. Dimethyl-isophthalic acid.

(*a*)-Cumidic acid. Mol. w. 194. [above 320°]. Formed by heating di-bromo-*m*-xylene dissolved in ether under pressure with ClCO.Et and sodium-amalgam. Formed also, together with (*β*)-cumidic acid, by oxidation of durene with dilute HNO₃ or of durylic acid with KMnO₄ (Schnapsauff,

B. 19, 2508). Minute prisms (from water) or plates (by sublimation).—BA" 1; aq: crystals, v. sol. water. Yields *m*-xylene on distilling with lime.

Methyl ether Me₂A". [76°]. Crystals.

***m*-Xylene dicarboxylic acid**

C₈H₆Me₂(CO₂H)₂ [1:3:4:5]. Dimethyl-phthalic acid. Isocumidic acid. [280°]. Formed by oxidation of (*β*)- and (*γ*)-isodurylic acid (Jacobsen, *B.* 15, 1857). Small crystals. May be sublimed. Yields *m*-xylene on distillation with lime. The Ca salt crystallises in small plates. The Ba salt is amorphous.

***p*-Xylene dicarboxylic acid**

C₈H₆Me₂(CO₂H)₂ [1:4:2:5]. Di-methyl-terephthalic acid. (*β*)-Cumidic acid. Formed, together with (*α*)-cumidic acid, by oxidation of *s*-durene with dilute HNO₃ or of durylic acid with KMnO₄ (S.). Minute six-sided prisms (from alcohol). Sublimes in small plates without melting. Nearly insol. hot water. Yields *p*-xylene on distilling with lime.—BA" 2; aq: tables, v. sol. water.

Methyl ether Me₂A". [114°]. (c. 297° cor.).

Xylene dicarboxylic acid

C₈H₆Me₂(CO₂H)₂.CH₂.CO₂H [3:2:1]. [178°]. Formed by oxidation of C₈H₇Me(CO₂Et)CH₂.CO₂H (Béhal a. Auger, *C. R.* 109, 972). Gives off CO₂ on fusion.

Xylene di-*o*-carboxylic acid v. PHENYLENE-DICARBOXYLIC ACID.

Reference.—OXY-XYLENE CARBOXYLIC ACID.

XYLENE GLYCOL v. DI-OXY-XYLENE.

***o*-XYLENE DIHYDRIDE v. CANTHARENE.**

***m*-Xylene dihydride** C₈H₁₀ (133°). S.G. 22.828. V.D. 3.74 (calc. 3.88). ρ_n 1.4075. Formed, together with a polymeride C₁₆H₁₄, (280°–285°) S.G. 22.832, by heating the ketone C₈H₆O with ZnCl₂. The ketone itself is obtained by distilling the anhydride C₈H₆O, which is got by the action of Ac₂O on cineolic acid, formed by oxidation of eucalyptol (Wallach, *A.* 258, 827). Liquid, smelling like xylene. Yields, on nitration C₈H₇Me₂(NO₂)₂ [1:3:4].

***p*-Xylene dihydride** OMe<CH₂.CH₂>OMe. CH₂.CH

(134°) at 720 mm. Formed by heating di-methyl-quinite dibromide C₈H₄Br₂ with quinoline (Baeyer, *B.* 25, 2122). Smells like turpentine. Forms a crystalline compound with HBr.

***m*-Xylene tetrahydride** C₈H₁₂Me₂. (119°). S.G. 22.814; ρ_n 1.794.

Formation.—1. By heating oxycamphoric anhydride C₁₀H₈O₄ with water at 180° or with H₂O at 150° (Wreden, *A.* 163, 386).—2. By heating camphoric acid with syngas phosphoric acid at 200°.—3. By distilling camphoric acid with ZnCl₂ (Ballo, *A.* 197, 322).—4. By heating camphoric acid with HIAq at 200° (Wreden, *A.* 187, 171).

Properties.—Oil. Oxidised by chromic acid mixture to acetic, isobutylic, isophthalic, and terephthalic acids. HNO₃ forms tri-nitro-*m*-xylene.

Xylene tetrahydride C₈H₁₂. (181°). S.G. 22.816. Occurs among the products of the distillation of colophony (Renard, *A. Ch.* [6] 1, 236). Slightly dextrorotatory liquid. Yields oily di- and tri-bromo-derivatives. Sulphuric acid forms an oily polymeride C₈H₁₂, which is oxidised by fuming HNO₃ to succinic and oxalic acids. Absorbs oxygen. Does not reduce

ammoniacal AgNO_3 . In ethereal solution it combines with Br, forming $\text{C}_8\text{H}_8\text{Br}_2$.

***m*-Xylene tetrahydride** (?) C_8H_{10} . (120°). *Octonaphthylene*. Formed by the action of moist Ag_2O on $\text{C}_8\text{H}_8\text{I}_2$, which is got by the action of CaI_2 at 60° on $\text{C}_8\text{H}_8\text{Cl}_2$ (175°), a product of the chlorination of octonaphthene (Jaskowkin, *J. R.* 16, ii. 294). Oil, smelling like turpentine. Combines with Br (2 atoms). An isomeric octonaphthylene (123°–129°) is got by distilling $\text{C}_8\text{H}_8\text{Cl}_2$ obtained by chlorination of iso-octonaphthene (Futochin, *J. R.* 16, ii. 295).

***m*-Xylene hexahydride** C_8H_{12} , i.e. $\text{C}_8\text{H}_8\text{Me}_2$ (1.3). *Octonaphthene*. (118°). S.G. $\frac{1}{4}$ 7814 (Lossen, *A.* 225, 110); $\frac{1}{4}$ 7706 (A.). C.E. (0°–26°) 001072. V.D. 3.87. S.V. 164.8. $\mu_D = 1.419$ at 22° (Wallach, *B.* 25, 923). Occurs in Baku petroleum (Beilstein & Kurbatoff, *B.* 13, 1820; Markownikoff & Spady, *B.* 20, 1850), and among the products of the distillation of coophony (Renard, *A. Ch.* [6] 1, 229). Formed by heating heptanaphthene carboxylic acid with HIAg and P (Aschan, *B.* 24, 2718). Prepared by heating camphoric acid or *m*-xylene with HIAg at 200° (Wreden, *A.* 187, 557). Liquid. Not oxidised by aqueous KMnO_4 , H_2SO_4 , and HNO_3 form tri-nitro-*m*-xylene. Sulphur at 220° forms *m*-xylene.

Isomeride C_8H_{12} . *Iso-octonaphthene*. (122°). S.G. $\frac{1}{4}$ 7767 $\frac{17}{10}$ 7637. Occurs in Caucasian petroleum (Futochin, *J. R.* 16, ii. 295). Liquid.

***p*-Xylene hexahydride** $\text{C}_8\text{H}_{12}\text{Me}_2$ (1.4). (138° cor.). V.D. 4.01 (obs.). S.G. $\frac{1}{4}$ 7956. Formed by heating bromo-camphor with ZnCl_2 (R. Schiff, *B.* 13, 1407; *G.* 10, 320). Liquid, yielding tri-nitro-*p*-xylene [127°] on nitration.

***m*-XYLENE PHOSPHINIC ACID**

Chloride $\text{C}_8\text{H}_8\text{Me}_2\text{PCl}$ (1.34). (257°). Got from mercuric dixyl $\text{Hg}(\text{C}_8\text{H}_8\text{Me}_2, 4:1:3)_2$ and PCl_5 at 235° (Weller, *B.* 20, 1720). Liquid, converted by water into the acid $\text{C}_8\text{H}_8\text{Me}_2\text{P}(\text{OH})_2$. Chlorine forms the compound $\text{C}_8\text{H}_8\text{Me}_2\text{PCl}_2$, which is converted by water into $\text{C}_8\text{H}_8\text{Me}_2\text{P}(\text{OH})_2$, (194°).

***m*-Xylene-phosphinic acid** $\text{C}_8\text{H}_8\text{Me}_2\text{P}(\text{OH})_2$, [98°] (Michaelis, *A.* 212, 237). Formed by the action of water on the chloride. Needles (from alcohol). Probably a mixture.

Chloride $\text{C}_8\text{H}_8\text{Me}_2\text{PCL}$ (256°). S.G. $\frac{1}{4}$ 1.24. Formed from *m*-xylene, PCl_5 , and AlCl_3 (Weller, *B.* 20, 1720). It is a mixture of the preceding body and the 1,3,5 isomeride. Readily absorbs chlorine, forming $\text{C}_8\text{H}_8\text{Me}_2\text{PCL}_2$, whence SO_2 forms $\text{C}_8\text{H}_8\text{Me}_2\text{POCl}$ (280°–300°).

***p*-Xylene phosphinic acid** $\text{C}_8\text{H}_8\text{Me}_2\text{P}(\text{OH})_2$. ***p*-Xylene phosphinous acid**. Formed by treating the chloride with hot water (Weller, *B.* 21, 1494). Crystallises with difficulty.

Chloride $\text{C}_8\text{H}_8\text{Me}_2\text{PCL}$ [–80°]. (254°). S.G. $\frac{1}{4}$ 1.25. Formed by heating *p*-xylene (150 g.) with AlCl_3 (80 g.) and PCl_5 (200 g.) for 36 hours with inverted condenser (Michaelis & Pansack, *A.* 212, 236). Strongly refracting liquid.

m*-XYLENE c-*PHOSPHONIC ACID

***C*-Xylene (a)-phosphinic acid** $\text{C}_8\text{H}_8\text{Me}_2\text{P}(\text{OH})_2$. ***m*-Xylene (a)-phosphinic acid**. (194°). S. 1.5 at 20°; 6.9 at 100°. Formed by boiling the chloride $\text{C}_8\text{H}_8\text{Me}_2\text{PCL}$ (v. *supra*) with water (Weller, *B.* 20, 1721). Needles, v. s. sol. alcohol. Decomposed into *m*-xylene

and phosphoric acid on heating with alkalis. Br added to dilute solutions forms bromo- and di-bromo-*m*-xylene. Yields two nitro-derivatives [182°] and [100°].

Salts. — BaA aq. Plates. — CdH_2A aq. Plates, more sol. cold than hot water. — NiH_2A aq. — Ag_2A : white pp.

***m*-Xylene s-phosphinic acid** $\text{C}_8\text{H}_8\text{Me}_2\text{PO}(\text{OH})_2$. ***m*-Xylene (b)-phosphinic acid**. [161°]. S. 1.8 at 15°; 117.8 at 100°. Prepared by boiling with water the mixture of chlorides $\text{C}_8\text{H}_8\text{Me}_2\text{POCl}_2$ (280°–300°) which is got by the action of SO_2 on the mixture of tetrachlorides $\text{C}_8\text{H}_8\text{Me}_2\text{PCL}_2$ formed by combination of chlorine with the mixture of chlorides $\text{C}_8\text{H}_8\text{Me}_2\text{PCL}$ obtained by heating *m*-xylene with PCl_5 and AlCl_3 (W.). Plates or needles, v. s. sol. alcohol and ether. Decomposed by alkalis into *m*-xylene and phosphoric acid.

***p*-Xylene phosphinic acid** $\text{C}_8\text{H}_8\text{Me}_2\text{PO}(\text{OH})_2$. [180°]. Formed by the action of water on $\text{C}_8\text{H}_8\text{Me}_2\text{PCL}$ [c. 60°] which is got by passing Cl_2 through the product of the action of PCl_5 on *p*-xylene in presence of AlCl_3 (Weller, *B.* 21, 1494). Needles, m. sol. water, v. sol. alcohol, al. sol. ether. Conc. HNO_3 forms the compound $\text{C}_8\text{H}_8(\text{NO}_2)_3\text{PO}(\text{OH})_2$, [224°]. KMnO_4 yields $\text{C}_8\text{H}_8\text{Me}(\text{CO}_2\text{H})_2\text{PO}_2\text{H}$, [278°].

Salts. — KHA — BaA . Pearly plates, more sol. cold than hot water.

Chloride $\text{C}_8\text{H}_8\text{Me}_2\text{POCl}_2$. (281°). S.G. $\frac{1}{4}$ 1.31. Oil. Formed by the action of SO_2 on $\text{C}_8\text{H}_8\text{Me}_2\text{PCL}$.

REFERENCE.—NITRO-XYLENE PHOSPHONIC ACID.

XYLENE PHTHALOYLIC ACID v. PHTHALYL KETONE CARBOXYLIC ACID.

***o*-Xylene sulphonic acid** $\text{C}_8\text{H}_8\text{SO}_3$, i.e. $\text{C}_8\text{H}_8\text{Me}_2\text{SO}_3\text{H}$ (1.24). [83°]. Formed by the action of zinc-dust on *o*-xylene sulphochloride (Jacobsen, *B.* 10, 1011). Plates (from water).

***m*-Xylene sulphonic acid** $\text{C}_8\text{H}_8\text{Me}_2(\text{SO}_3\text{H})$ (1.34). [c. 50°]. Formed by reducing the sulphonic chloride $\text{C}_8\text{H}_8\text{Me}_2\text{SO}_2\text{Cl}$ (Jacobsen; cf. Lindoff & Otto, *A.* 146, 233). Crystalline.

***p*-Xylene sulphonic acid** $\text{C}_8\text{H}_8\text{Me}_2(\text{SO}_3\text{H})$ (1.42). [85°]. Groups of needles (Jacobsen, *B.* 11, 22).

***o*-Xylene sulphonic acid** $\text{C}_8\text{H}_8\text{SO}_3$, i.e. $\text{C}_8\text{H}_8\text{Me}_2(\text{SO}_3\text{H})$ (1.24). Formed by warming *o*-xylene with H_2SO_4 (Jacobsen, *B.* 10, 1011; 11, 22). Tables (containing 2aq) (from dilute H_2SO_4). — NaA 5aq. — BaA 2aq. S. 5.8 at 0°; 33.6 at 100°.

Chloride $\text{C}_8\text{H}_8\text{Me}_2\text{SO}_2\text{Cl}$ [52°]. Prisms. **Amide** $\text{C}_8\text{H}_8\text{Me}_2\text{SO}_2\text{NH}_2$ [144°]. Yields two acids $\text{C}_8\text{H}_8\text{Me}(\text{CO}_2\text{H})_2\text{SO}_2\text{NH}_2$ on oxidation by KMnO_4 .

***o*-Xylene c-sulphonic acid** $\text{C}_8\text{H}_8\text{Me}_2\text{SO}_3\text{H}$ (1.23). Formed by the action of sodium amalgam on $\text{C}_8\text{H}_8\text{Me}_2\text{Cl}(\text{SO}_3\text{H})$ [1:2:3:3] (Krüger, *a.B.* 18, 1760).

Amide $\text{C}_8\text{H}_8\text{Me}_2\text{SO}_2\text{NH}_2$. Granules.

***m*-Xylene c-sulphonic acid** $\text{C}_8\text{H}_8\text{Me}_2(\text{SO}_3\text{H})$ [1:3:2]. ***m*-Xylene (b)-sulphonic acid**. Formed, together with a larger quantity of the (1,3,4)-isomeride, by dissolving *m*-xylene in fuming H_2SO_4 (Jacobsen, *A.* 184, 183; *B.* 11, 18). It remains in the acid liquor after pptg. the (1,3,4)-isomeride by the proper quantity of water. Potash-fusion yields *p*-xylenol [74.5°] (Jacobsen, *B.* 21, 3228). Its K salt heated with sodium

formate forms an acid $C_6H_4O_2$ [99°].— KA' .
 BaA' : minute needles.— CaA' : aq.

Chloride $C_6H_4Me_2SO_2Cl$. Oil.

Amide $C_6H_4Me_2SO_2NH_2$ [98°]. Needles.

m-Xylene sulphonic acid $C_6H_4Me_2(SO_3H)$ [1:3:4]. *m*-Xylene (a)-sulphonic acid. Formed as above. Long flat prisms (containing 2aq). Its K' salt heated with sodium formate yields xylylic acid.— NaA' .— BaA' . Small plates.— CaA' , 9aq.— CaA' , 6aq.

Chloride $C_6H_4Me_2SO_2Cl$ [34°].

Amide [137°]. Needles (from water).
 $3zCl$ at 160° forms $C_6H_4Me_2SO_2NHBz$ [151°] Mahon, *Am.* 4, 194, which yields crystalline $3a(C_6H_4N_2SO_2)_2$ aq and BaA' , sl. sol. water.

p-Xylene sulphonic acid $C_6H_4Me_2(SO_3H)$ [1:4:2]. Formed by sulphonating *p*-xylene (Beilstein a. Wahlfors, *A.* 133, 38; Fittig a. Glinzer, *A.* 136, 305; Jacobsen, *B.* 10, 1009; 11, 22; Remsen a. Emerson, *Am.* 8, 265). Plates or prisms (containing 2aq). Oxidised by alkaline $KMnO_4$ to sulpho-terephthalic and two sulpho-*p*-toluic acids.— NaA' aq. [148°]. Trimetric plates; $a:b:c = 1.077:1.1498$ (Moody a. Nicholson, *C. J.* 57, 978).— KA' aq.— BaA' , S. 2-27 at 0°; 5-53 at 100°.— CaA' , 8aq. Light-blue triclinic prisms.— ZnA' , 10aq.

Chloride $C_6H_4Me_2SO_2Cl$ [26°]. Prisms.

Amide [148°]. Needles, m. sol. hot water.

o-Xylene disulphonic acid $C_6H_4Me_2(SO_3H)_2$. Formed by heating (1,2,4)-xylene sulphonic acid with $ClSO_3H$ at 150° (Pfannenstill, *J. pr.* [2] 46, 155).— KA' aq.— BaA' 3aq.— PbA' 3aq. Prisms.

Chloride $C_6H_4Me_2(SO_2Cl)_2$ [79°]. Prisms.

Amide $C_6H_4Me_2(SO_2NH_2)_2$ [239°].

m-Xylene disulphonic acid $C_6H_4Me_2(SO_3H)_2$ [1:3:4:2]. Formed by heating *m*-xylene with fuming H_2SO_4 at 150° (Wischin, *B.* 23, 2113), and by heating (1,3,4)-xylene sulphonic acid with SO_3 at 150° (P.). Deliquescent needles, converted by potash-fusion into $C_6H_4Me_2(OH)_2$ [146°].— $(NH_4)A'$.— $NaHA'$ 3aq.— KA' 2aq.— BaA' 3aq. Needles, v. sol. water.— PbA' 3aq.— CaA' . Gummy mass.

Ethyl ether EtA'. Plates.

Chloride $C_6H_4Me_2(SO_2Cl)_2$ [129°]. Converted by PCl_5 at 180° (2,4,1,3)-di-chloro-xylene. (220°).

Amide $C_6H_4N_2S_2O_4$ [240°]. Needles.

Oxidised by $KMnO_4$ to $C_6H_4(<SO_2>NH_2)$ [225°].

Ethylamide $C_6H_4Me_2(SO_2NHEt)_2$ [135°].

m-Xylene disulphonic acid $C_6H_4Me_2(SO_3H)_2$ [1:3:2:6?]. Formed in small quantity, together with the preceding isomeride, by heating (1,3,2)-xylene sulphonic acid with $ClSO_3H$ at 150° (Pfannenstill, *J. pr.* [2] 46, 154). Needles.

Chloride $C_6H_4Me_2(SO_2Cl)_2$. Oil.

Amide. [210°]. More sol. water than its isomeride.

p-Xylene disulphonic acid $C_6H_4Me_2(SO_3H)_2$ [1:4:2:6?]. Formed by heating (1,4,2)- $C_6H_4Me_2(SO_2Cl)_2$ with fuming H_2SO_4 (Holmes, *Am.* 13, 372; Pfannenstill, *J. pr.* [2] 46, 156). Needles, v. a. sol. water.— BaA' 3aq.— CaA' 4aq.— MgA' 7aq.— PbA' 3aq.— AgA' 4aq.

Chloride $C_6H_4Me_2(SO_2Cl)_2$ [78°].

Amide $C_6H_4Me_2(SO_2NH_2)_2$ [295°].

References.—Bromo-, Bromo-nitro-, Nitro- and Nitro-amido-, Xylene sulphonic acid.

XYLENE THIOSULPHONIC ACID. $Xylyl$ ether $C_6H_4SO_2S.C_6H_5$. *Xylyl disulphide*.

Formed by heating xylene sulphonic acid with water at 150°–160° (Otto a. Lindorf, *A.* 146, 289). Oil, v. sol. alcohol and ether.

XYLENIC ALCOHOL is TOLYL-CARRINOL.

XYLENIC DIBROMIDE v. Di-*o*-BROMOXYLENE.

XYLENIC GLYCOL v. Di-*o*-OXYXYLENE.

o-XYLENOL C_6H_4O i.e. $C_6H_4Me_2OH$ [1:2:4]. Mol. w. 122. [62°]. (225° i.v.). H.F.p. 61,566 (Stohmann, *J. pr.* [2] 34, 816). Obtained by potash-fusion from the sulphenic acid (Jacobsen, *B.* 11, 238), and by the diazo-reaction from (1,2,4)-xylylidine (Jacobsen, *B.* 17, 161). Long needles (from water). $SiCl_4$ yields $Si(OC_6H_4)_2$, crystallising in prisms (350°–360° at 120 mm.) (Hertkorn, *B.* 18, 1681). Ammoniacal $ZnBr_2$ at 800° from xylylidine and dicyllamine.— $NaOC_2H_5$. Flat needles, v. sl. sol. $NaOH$ aq.

Benzoyl derivative [57°]. H.F. 77,768 (Stohmann, *J. pr.* [2] 36, 8).

o-Xylenol $C_6H_4Me_2(OH)$ [1:2:3]. [75°]. (218° i.v.). Occurs in coal-tar (Schulze, *B.* 20, 410). Formed by the action of nitrous acid on *o*-xylylidine (Töhl, *B.* 18, 2562; Nöling a. Forel, *B.* 18, 2673). Slender needles. Its aqueous solution gives a blue colour with $FeCl_3$.
c-m-Xylenol $C_6H_4Me_2(OH)$ [1:3:2]. [49°]. Obtained from the crude xylylidine, or by the action of HCl on *p*-oxy-mesitylenic acid (Nöling; Jacobsen, *B.* 21, 2829). *p*-Xylenol is got instead of *m*-xylenol by potash-fusion from (1,3,2)-xylene sulphonic acid (Jacobsen, *B.* 11, 26; 21, 2328).

m-Xylenol $C_6H_4Me_2(OH)$ [1:3:4]. [26°] (Jacobsen, *B.* 18, 3463); [73°] (Staedel a. Holz, *B.* 18, 2919). (211° i.v.). S.G. 2.10862. H.F.p. 59,501 (Stohmann, *J. pr.* [2] 34, 316).

Formation.—1. From *m*-xylene sulphonic acid by potash-fusion (Jacobsen, *B.* 11, 24, 375; cf. Wroblewski, *B.* [2] 10, 286; Warts, *J.* 1868, 459). 2. By heating oxy-mesitylenic acid with conc. HCl aq at 200° (Jacobsen, *B.* 11, 2052). 3. By reduction of nitro-*m*-xylene and treatment of the resulting xylylidine with nitrous acid (Harmsen, *B.* 13, 1558; S. a. S.; Hodgkinson a. Limpach, *C. J.* 63, 104).

Properties.—Needles, v. sl. sol. water, miscible with alcohol and ether. Volatile with steam. $FeCl_3$ colours its aqueous solution blue and its alcoholic solution green, being changed to bright blue on dilution with water. Yields the corresponding xylylidine and di-xylylamine when heated with $ZnBr_2$, $SnCl_4$, and NH_4Br at 315° (Müller, *B.* 20, 1041). Potash-fusion forms (4,1,3)-oxytoluic acid. Yields oily $P(OC_6H_4)_3$ (Kreysler, *B.* 18, 1703). $SiCl_4$ forms $Si(OC_6H_4)_2$ (455°) (Hertkorn, *B.* 18, 1690).

Salt.— $NaOC_2H_5$, v. sol. water and conc. $NaOH$ aq (dullish Na salts of other xylenols).

Methyl ether $MeOC_6H_4$, (192° i.v.) (J.). (186°) (S.). H.F.p. 46,336 (Stohmann, *J. pr.* [2] 35, 24).

Acetyl derivative C_6H_4OAc . (226° i.v.).

o-Xylenol $C_6H_4Me_2(OH)$ [1:3:5]. [84°] (T.); [68°] (N. a. F.). Occurs in coal-tar (Schulze, *B.* 20, 410). Formed by the action of nitrous acid on *o*-xylylidine (Töhl, *B.* 18, 262; Nöling a. Forel, *B.* 18, 2679). Slender needles (from

water). Not coloured by FeCl_3 — NaOAc , H_2O . Plates, sl. sol. NaOH aq.

p-Xylenol $\text{C}_6\text{H}_4(\text{OH})_2$ [1:4:2]. [74:5°]. (211.5° i.v.). H.F.p. 61,362 (Stohmann, *J. pr.* [2] 84, 816). S.G. 24 0.971. Formed by potash-fusion from *m*- and from *p*-xylene sulphonic acid and from oxy-mesitylenic acid (Wurtz, *A.* 147, 878; Jacobsen, *B.* 11, 426). Formed also from *p*-xylydine by diazotisation followed by boiling with water (Nölting, Witt, a. Forel, *B.* 18, 2665). Long flat needles (from dilute alcohol). Volatile with steam. Its aqueous solution is not coloured by FeCl_3 .

Potash-fusion gives (3,4,1)-oxy-toluic and oxy-terephthalic acid. KNO_3 and HOAc yield a nitroso-derivative $\text{C}_6\text{H}_3\text{Me}_2(\text{OH})(\text{NO})$ [1:4:3:6] [163°], which is the oxim of *p*-xyloquinone (Oliveri, *G.* 12, 162; Goldschmidt a. Schmid, *B.* 18, 568).

Salt.— NaOAc , H_2O . Large plates, sl. sol. cold NaOH aq.

Methyl ether MeOC_6H_4 . (194° i.v.). Oil. *Ethyl ether* EtOC_6H_4 . (199°) (S.); (205°) (N. W. a. F.). Oil. H.F.p. 54, 150.

Acetyl derivative $\text{C}_6\text{H}_3\text{Me}_2\text{OAc}$. (237° i.v.). S.G. 4 1.0264. Oil, not solid at -20°.

Xylenol. (220°). Occurs in beechwood-tar (Marasse, *A.* 152, 75; Tiemann a. Mendelssohn, *B.* 10, 57). Oil. Yields $\text{C}_6\text{H}_4\text{OMe}$ (220°). On boiling with aqueous KMnO_4 it yields an acid which is converted by potash-fusion into *u*-oxyisophthalic acid [300°].

References.—Bromo- and Nitro-XYLENOLS. **XYLENOLIC ACID** v. OXY-DI-METHYL-BENZOIC ACID.

O-XYLENOL SULPHONIC ACID $\text{C}_6\text{H}_4(\text{SO}_3\text{H})_2$, i.e. $\text{C}_6\text{H}_3\text{Me}_2(\text{OH})\text{SO}_3\text{H}$. Formed by sulphonation of (1,2,4)-xylenol (Jacobsen, *B.* 11, 24). FeCl_3 gives a violet colour in neutral solutions.— NaA . Slender prisms or small laminae.— BA . Nodular groups of minute laminae, sl. sol. cold water.

m-Xylenol (α)-sulphonic acid. Formed, together with the (β)-isomeride, by dissolving (1,3,4)-xylenol in H_2SO_4 (J.). FeCl_3 gives a violet-blue colour.— NaA . Tables.— KA . Plates.— BA . Leaflets.

m-Xylenol (β)-sulphonic acid $\text{C}_6\text{H}_3\text{Me}_2(\text{OH})\text{SO}_3\text{H}$ [1:3:4:2] (Jacobsen, *A.* 195, 283). Formed as above. Coloured violet-blue by FeCl_3 . Converted by potash-fusion into (2,5,1)-oxy-toluic acid.— NaA 4aq. Laminae.— BA . Minute needles, less soluble than the Ba salt of the (α)-acid. By sulphonating (1,3,4)-xylenol by ClSO_3H , Hodgkinson (*C. J.* 62, 110) obtained a xylenol sulphonic acid yielding BA , aq.

m-Xylenol sulphonic acid $\text{C}_6\text{H}_3\text{Me}_2(\text{OH})\text{SO}_3\text{H}$ [1:3:4:4]. Formed from $\text{C}_6\text{H}_3\text{Me}_2(\text{NH}_2)\text{SO}_3\text{H}$ by the diazo-reaction (Sartig, *A.* 280, 886). Slender needles, v. sol. water and alcohol. The acid and its salts give with FeCl_3 a bluish-violet colour turned green by alcohol.— KA .— BA , aq. Needles, v. e. sol. water.— PbA , 2aq.

Ethyl derivative $\text{C}_6\text{H}_3\text{Me}_2(\text{OEt})\text{SO}_3\text{H}$. Formed by heating diazo-*m*-xylene sulphonic acid with alcohol under pressure. Minute tables, v. sol. water and alcohol.— BA , 3aq. Minute plates, v. sol. water.

p-Xylenol sulphonic acid. Formed by dissolving *p*-xylenol in warm H_2SO_4 . Hydrated

leaflets.— NaA 5aq. Tables.— BA . Minute needles.

Reference.—NITRO-XYLENOL SULPHONIC ACID. **XYLENYL-AMIDOXIM** v. DI-METHYL-BENZOIC ACID.

XYLENYL ALCOHOL v. DI-OXY-XYLENE. **XYLENYL CHLORIDE** v. TETRA-*o*-CHLOROXYLENE.

XYLETIC ACID is OXY-DI-METHYL-BENZOIC ACID.

XYLIC ACID is DI-METHYL-BENZOIC ACID.

XYLIDIC ACID is TOLUENE DICARBOXYLIC ACID.

c-o-XYLIDINE $\text{C}_6\text{H}_4\text{Me}_2(\text{NH})$ [1:2:3].—*Di-methyl-phenyl-amine*. *Amido-xylylene*. Mol. w. 121. (223° i.v.) at 739 mm. S.G. 12 0.991. Obtained by reducing di-*o*-bromo-*o*-xylydine $\text{C}_6\text{H}_2\text{Br}_2(\text{NH})$ [1:2:4:5:3] with sodium-amalgam in the cold (Töhl, *B.* 18, 2562). Got also by heating (1,2,4)-xylenol with NH_4Br and ammonio-zinc bromide at 300° (Müller, *B.* 20, 1039). Prepared from *o*-xylylene by nitration and reduction (Nölting a. Forel, *B.* 18, 2671; Wroblewski, *B.* 18, 2904). Oil. When oxidised by $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 it yields a small quantity of *o*-xyloquinone [55°]. Converted by the diazo-reaction into *o*-xylenol [73°]. H_2SO_4 and HNO_3 give (4,1,2,3)-nitro-xylydine [114°] and (6,1,2,3)-nitro-xylydine [65°] (Nölting a. Stoecklin, *B.* 24, 567).—Salts: BHCl aq. Plates. Begins to sublime at 100°.— BHNO_3 . Needles.— $\text{B}_2\text{H}_2\text{SO}_4$. Large plates, sl. sol. water.

Acetyl derivative $\text{C}_6\text{H}_3\text{Me}_2\text{NHAc}$. [134°] (N. a. F.); [131°] (L.; W.). Slender needles.

i-o-Xylydine $\text{C}_6\text{H}_3\text{Me}_2(\text{NH})$ [1:2:4]. [49°]. (226°). S.G. 12 1.0755. Prepared from *o*-xylylene by nitration and reduction (Jacobsen, *B.* 17, 159). Got also by heating *m*-toluidine hydrochloride with MeOH at 300° (Limpach, *B.* 21, 643). Monoclinic crystals, not coloured by exposure to light and air. Gives no colour with bleaching powder. Its solutions colour pine-wood yellow. On nitration it yields (6,1,2,4)-nitro-xylydine [137°] and an isomeride [80°] (N. a. S.). Yields a saffranine on oxidation together with di-amido-di-phenyl-amine (Nietzki, *B.* 19, 3163).—Salt: BHCl aq. Prisms, v. sol. water. Yields ψ -cumidine when heated with MeOH at 310° (N. a. F.).

Acetyl derivative $\text{C}_6\text{H}_3\text{Me}_2\text{NHAc}$. [99°]. *c-m*-Xylydine $\text{C}_6\text{H}_3\text{Me}_2(\text{NH})$ [1:3:2]. (S).

Xylydine (214° i.v.) at 739 mm. (N. a. F.). S.G. 22 0.9942 (W.). Formed by distilling *p*-amido-mesitylenic acid with lime (Schmitz, *A.* 193, 179) and by reducing *c*-nitro-*m*-xylylene (Grövingk, *B.* 17, 2430). Obtained from commercial xylydine by crystallisation of the sulphate; the last mother-liquor depositing crystals which are converted into the acetyl derivative by distillation with HOAc . The acetyl derivative is saponified by treatment with dilute (25 p.c.) H_2SO_4 (Nölting a. Pick, *B.* 21, 3150; cf. Wroblewski, *B.* 12, 1226). Gives *m*-xyloquinone [73°] on oxidation (Nölting a. Forel, *B.* 18, 2676). Yields (4,1,3,2)-nitro-xylydine [82°] on nitration (Nölting a. Stoecklin, *B.* [3] 6, 381).—Salts: BHCl — BHCl aq. S. 9.7 at 18°. Monoclinic plates. Yields mesidine on heating with MeOH at 310°.— BHNO_3 . S. 6.2. Needles.— $\text{B}_2\text{H}_2\text{SO}_4$. Very soluble needles.— $\text{B}_2\text{H}_2\text{SO}_4$, 2aq. S. 60.

Acetyl derivative $C_9H_8Me_2NH_2$ [174°] (G.); [176°] (N. a. F.). Needles.

Benzoyl derivative $C_9H_7Me_2NHC_6H_5$ [140°]. Needles. Yields benzoyl-nitro-xylylidine [178°] on nitration (Hübner, A. 208, 818).

***m*-Xylylidine** $C_8H_7Me_2(NH_2)$ [1:3:5]. (222° I.V.). S.G. 1.5. 972. Formed by reduction of *s*-nitro-*m*-xylene [71°] (Thöl, B. 18, 362; Nölting a. Forel, B. 18, 2678). On oxidation by $K_2Cr_2O_7$ and H_2SO_4 it gives *m*-xyloquinone [73°]. By boiling the diazo-compound with water-xylenol [68°] is formed. $ClCO_2Et$ forms $C_8H_7Me_2NH.CO_2Et$ [77-5°] (Frentzel, C. C. 1888, 1361).— B^*HCl . $MeOH$ at 250°–300° yields isocumidine $C_8H_7Me_2(NH_2)$ [5:4:3:1] (Limpach, B. 21, 643).— $B^*H_2SO_4$ aq.— B^*HNO_3 S. 4:66 at 13°.

Acetyl derivative $C_9H_8Me_2NH_2$ (N. a. F.); [138°] (T.); [144-6°] (W.). Colourless plates (from alcohol or ether).

***i*-m-Xylylidine** $C_8H_7Me_2(NH_2)$ [1:3:4]. (a). Xylylidine. (215°) at 745 mm. (G.). S.G. 1.5. 9184 (H.). S.V. 1483.

Formation.—1. By reducing *i*-nitro-*m*-xylene (Deumelandt, A. 144, 273; Tavildaroff, B. 2, 553; Wroblewski, A. 192, 215; 207, 91; Grevingk, B. 17, 2430; Wallach, A. 258, 331). It may be isolated from commercial xylylidine by conversion into hydrochloride and several crystallisations from water; the yield being about 40 p.c. (Nölting a. Forel, B. 18, 2677).—2. By heating *o*- and *p*-toluidine hydrochloride with $MeOH$ at 300° (Hofmann, B. 9, 1295; Limpach, B. 21, 640).—3. By distilling (4,3,1,5)-amidomesitylic acid with lime (Schmitz, A. 193, 177).—4. By heating *i*-m-xylylidine with ammonium-zinc bromide and NH_4Br (Müller, B. 20, 1039).

Reactions.—1. When dissolved in H_2SO_4 (10 pts.) it yields $C_8H_7Me_2(NH_2)(NO_2)$ [1:3:4:6] [123°] on nitration (Nölting a. Collin, B. 17, 265).—2. The hydrochloride heated with $MeOH$ at 310° yields mesidine.—3. $ClCO_2Et$ forms $C_8H_7Me_2NH.CO_2Et$ [57°] (Frentzel, C. C. 1888, 1361).—4. When mixed with di-amido-di-phenylamine it yields a saffranine on oxidation (Nietzki, B. 19, 8163).—5. When *m*-xylylidine (4 pts.) is heated with S (1 pt.) at 190° it gives off H_2S and forms a base $C_8H_7N_2S$ [107°] (285° at 14 mm.) which crystallises from alcohol in yellowish-white prisms and yields $C_8H_7N_2S$ [227°] (Anschütz a. Schultz, B. 22, 582). By further heating with sulphur a homologue of primuline is formed.—6. *Enanthol* forms oily C_8H_7NO (Leeds, B. 16, 288).—7. *Acrolein* yields C_8H_7N , a reddish-yellow mass which on distillation yields crypidine $C_{11}H_{11}N$ (270°) (Leeds, A. C. J. 5, 1).

• Salts.— B^*HCl . Monoclinic prisms.— B^*HCl aq. Plates (Staedel a. Holz, B. 18, 2849).— $B^*H_2PtCl_6$.— B^*HBr . Trimetric plates.— B^*HNO_3 .— $B^*H_2SO_4$ aq. Cubes. Losses xylylidine on evaporation of its solution (Nölting a. Pick, B. [2] 50, 606).— $B^*H_3PO_4$. Only phosphate formed (Lewy, B. 19, 2728).— $B^*H_2C_2O_7$ S. 8:32 at 18°.— B^*ZnCl_2 (Lachovitch, M. 9, 514).— $B^*HgH(SO_4)$ aq.— $B^*Cu_2H_2(SO_4)_2$ (Deniges, C. R. 112, 970).

Formyl derivative $C_8H_7Me_2NH.CO_2O$. [111°] (G.); [114°] (G. a. M.). Got by heating the base (12 g.) with formic acid (5 g.) at 150° (Gasiorowski a. Mers, B. 18, 1011; Gudemann,

B. 21, 2549). Crystals (from water). Converted by P_2S_5 at 100° into the thioformyl derivative [105°].

Bromo-acetyl derivative

$C_8H_7Me_2NHC_6H_4Br$. [129°]. Needles or plates (from dilute alcohol). P_2S_5 forms the compound $C_8H_7Me_2NH.CSMe$ [95°] (Jacobsen a. Ney, B. 22, 907).

Di-acetyl derivative $C_8H_7Me_2NAC_6H_4$. [60°]. Formed, together with the mono-acetyl derivative, by boiling the base with Ac_2O (Wallach, A. 258, 301).

Benzoyl derivative $C_8H_7Me_2NHC_6H_5$. [192°]. Needles (Hübner, A. 208, 818). Converted by HNO_3 into the nitro-benzoyl derivative [184°] which is reduced by tin and $HOAc$ to $C_8H_7Me_2NH > C_6H_5$ [195°].

Phthalyl derivative [158°]. Prisms (from alcohol).

***p*-Xylylidine** $C_8H_7Me_2(NH_2)$ [1:4:2]. [15-5°] (Michael, Z. 26, 39). (215° i.V.) at 739 mm. (N. a. F.); (213-5° uncor.) (M.); (220°) (S.). S.G. 1.5. 980. Obtained from *m*-xylene by nitration and reduction (Schaumann, B. 11, 1537; Nölting a. Forel, B. 18, 2664; 19, 2680). Occurs to the extent of about 25 p.c. in commercial xylylidine, from which it may be isolated by dissolving in warm H_2SO_4 and pouring into hot water. The sparingly soluble *m*-xylylidine sulphonic acid crystallises out, and the mother-liquor, after successive treatment with $CaCO_3$ and Na_2CO_3 , yields on evaporation sparingly soluble, pearly plates of sodium *p*-xylylidine sulphonate, which on distillation with lime give *p*-xylylidine almost without loss. May also be got from crude xylylidine by means of its benzylidene derivative.

Reactions.—1. Oxidised by $K_2Cr_2O_7$ and H_2SO_4 to *p*-xyloquinone [123°], the yield being 70 p.c.—2. Converted by the diazo-reaction into *p*-xylenol [75°] (210°).—3. On heating with sulphur it yields $C_8H_7N_2S$ [144°], which crystallises from alcohol in yellowish needles, and yields an acetyl derivative [212°] (Anschütz a. Schultz, B. 22, 585).—4. The hydrochloride heated with $MeOH$ at 290° under pressure forms ψ -cumidine (Limpach, B. 21, 646).—5. *Benzoin aldehyde* forms $C_8H_7Me_2N.CHPh$ [102°] (Pfug, A. 255, 166). The same body [98°] is got by adding benzoic aldehyde to an alcoholic solution of thionyl-*p*-xylylidine (Michaelis, A. 274, 237).

• Salts.— B^*HCl aq. Leaflets, subliming at 125°–130° in needles.— B^*HNO_3 . Needles.— $B^*H_2SO_4$. Plates, sl. sol. water.— $B^*H_2C_2O_7$.

Formyl derivative $C_8H_7Me_2NH.CO_2O$. [112°]. Needles (Pfug, A. 255, 168).

Acetyl derivative $C_8H_7Me_2NHC_6H_5$. [189°]. Prisms. Yields on nitration acetyl-nitro-*p*-xylylidine [192°].

Bromo-acetyl derivative

$C_8H_7Me_2NH.CO_2C_6H_4Br$. [145°]. Formed from bromo-acetyl bromide and *p*-xylylidine in benzene (Abenius, J. pr. [2] 40, 435). Needles (from dilute alcohol). Boiling alcoholic potash converts it into an azine and the compound $C_8H_7Me_2NH.CO_2CH_2.OEt$ [50°].

Oxalyl derivative $(C_8H_7Me_2NH.CO_2)_2O$. Formed by heating the oxalate at 130°. Needles, subliming at 125°. An oxalyl-xylylidine [204°] was obtained by Genz (B. 3, 227) from crude, commercial xylylidine.

Benzoyl derivative $C_6H_5Me.NHBz$. [140°]. Needles.

References.—BROMO-, CHLORO-, and NITROXYLIDINE.

XYLIDINE SULPHONIC ACID v. AMIDOXYLENE SULPHONIC ACID and BROMO- and NITROXYLIDINE SULPHONIC ACIDS.

XYLIDINIC ACID v. TOLUENE DICARBOXYLIC ACID.

XYLINDEIN. $C_{12}H_{10}O$. χ lyl. 4.7 p.s.; N, 1.0 p.c. A green colouring matter in green decayed wood (Bommier, *C. R.* 66, 103; Liebermann, *B.* 7, 1102). Extracted by phenol and p.p.d. by alcohol or ether. Four-sided blue plates, with coppery lustre. H_2SO_4 forms a green solution. Bideol (*C. N.* 53, 277) finds that the blue substance in decayed birch-wood is soluble in chloroform, while the blue resin obtained from coniferin by successive treatment with H_2SO_4 and water is insol. chloroform.

XYLITONE $C_{12}H_{10}O$. χ lyl. oil. (252°) (Pinner, *B.* 15, 594; 16, 1729) (c. 240°) (Claisen & Ehrhardt, *B.* 22, 1013). S.G. 935. A product of the action of HCl on acetone (P.). Formed also by the action of $NaOEt$ on methyl oxide in ether, and in the preparation of acetylacetone by the action of boiling $EtOAc$ and $NaOAc$ on acetone (C. a. E.). Oil, easily resinified by strong acids.

Dixylitone $C_{12}H_{10}O_2$. (310°–320°). A product of the action of HCl on acetone (Pinner).

XYLOHYDROQUINONE v. HYDROXYLOQUINONE.

XYLOIC ACID v. DI-METHYL-BENZOIC ACID.

XYLONIC ACID $C_8H_8O_4$. [α] = 17.48°. Formed by oxidising xylene with bromine (Tollens, *A.* 260, 367). Dextrorotatory. Its Ca , Zn , and Ag salts are amorphous. $—SrA_2$. [α]_D = +12.14°.

XYLONITRILE v. Nitrile of DI-METHYL-BENZOIC ACID.

o-XYLOQUINONE $C_8H_6O_2$, i.e. $C_6H_4Me_2$ [1:2:3:6]. [55°]. Formed by oxidation of o-xylidine by $K_2Cr_2O_7$ and H_2SO_4 , the yield being about 10 p.c. (Nörling & Forel, *B.* 18, 2678). Yellow needles (by sublimation), v. sl. sol. water, m. sol. alcohol and ether.

m-Xyloquinone $C_8H_6Me_2$ [1:3:2:5]. [78°]. Formed by oxidation either of m- or s-m-xylidine with $K_2Cr_2O_7$ and H_2SO_4 (Nörling & Forel, *B.* 18, 2679). Got also by oxidation of mesidine (Nörling & Baumann, *B.* 18, 1151). Yellow needles.

p-Xyloquinone $C_8H_6Me_2$ [1:4:2:5]. *Phlorone*. *Metaphlorone*. Mol. w. 136. [124°].

Formation.—1. Occurs, together with toluquinone and other bodies, among the products of the action of MnO_2 and H_2SO_4 on coal-tar and beechwood-tar (Bommier & Bouilhon, *J. R.* 55, 214; Görup-Besanez & vofj. Råd, *Z.* [2] 4, 560; Carstanjen, *J. pr.* [2] 23, 425).—2. By oxidation of p-xylene-diamine (Nietzki, *B.* 18, 472; A. 215, 168).—3. By oxidation of ψ -cumenol (Carstanjen, *J. pr.* [2] 23, 430f).—4. By oxidation of ψ -cumidine by CrO_3 (Nörling & Th. Baumann, *B.* 18, 1151; Sutkowski, *B.* 20, 977).—5. By distilling xylidine (218°) with H_2SO_4 and MnO_2 ; the yield being 5 p.c. (C.).—6. By oxidation of p-xylidine with $K_2Cr_2O_7$ and H_2SO_4 , the yield being over 70 p.c. (Nörling, Witt, & Forel,

B. 18, 2667).—7. By heating diacetyl with dilute $NaOHAq$ (Van Pechmann, *B.* 21, 1490).

Preparation.—1. Commercial xylene (180°–140°) is heated with H_2SO_4 at 100° for six days; the product poured into water; neutralised by $CaCO_3$; treated with K_2CO_3 ; and the K salts of the sulphonic acids fused with potash. The product is dissolved in water, acidified, and extracted with ether; and the mixture of xylenols so obtained is dissolved in warm H_2SO_4 , and then diluted with water and distilled with MnO_2 . Crystals of p-xyloquinone appear in the condenser and receiver (Carstanjen, *J. pr.* [2] 23, 427).—2. 'Yellow carboic acid' or 'creosote,' the mother-liquor from which phenol has crystallised, is dissolved in H_2SO_4 , diluted with water, and then distilled with MnO_2 . The solid found in the receiver is crystallised from alcohol when the first crop of crystals is xyloquinone (L. Carstanjen, *J. pr.* [2] 23, 423).

Properties.—Long yellow needles (from benzene), sl. sol. water and cold alcohol, v. sol. ether. May be sublimed. Volatile with steam.

Reactions.—1. Distilled with zinc-dust gives a hydrocarbon that oxidises to terephthalic acid.—2. Reduced by aqueous SO_2 to hydroxyloquinone.—3. Conc. HCl converts it into a mixture of mono- and di-chloro-hydro-xyloquinones, $C_8H_5ClMe_2(OH)$, [147°] and $C_8H_4Cl_2Me_2(OH)$, [175°].

Mono-oxim $C_8H_7Me_2O(NOH)$. *Nitroso-p-xyleneol*. [168°]. Formed by heating p-xyloquinone (2 pts.) with an alcoholic solution of hydroxylamine hydrochloride (1 pt.) (Goldschmidt & Schmid, *B.* 18, 568; Sutkowski, *B.* 20, 978). Obtained also by adding KNO_3 and excess of $HOAc$ to an alkaline solution of p-xyleneol (Oliveri, *G.* 12, 162). Yellowish needles (from alcohol), v. sol. alcohol, ether, and benzene, insol. cold water. Alkalis form a deep orange-red solution. Reduced by $SnCl_2$ to amido-p-xyleneol. Oxidised by alkaline K_2FeO_4 to nitro-p-xyleneol.

Di-oxim $C_8H_6Me_2(OH)_2$. [272°]. Formed by boiling the quinone (1 mol.) with an alcoholic solution of hydroxylamine hydrochloride (2 mols.) (Sutkowski, *B.* 20, 977). V. sl. sol. alcohol, acetic acid, and benzene, insol. water. Dissolves in alkalis with a yellow colour. By tin and HCl it is reduced to xylene-p-diamine. Its di-acetyl derivative $C_8H_4Me_4(NOAc)_2$ crystallises from acetic acid in small yellow prisms, [170°], v. sol. alcohol and benzene.

References.—DI-BROMO- and CHLOROXYLOQUINONE.

XYLORCIN v. DI-OXYXYLENE.

XYLOSE v. p. 538.

XYLOSTEIN. A glucoside in the berries of *Bonicera Xylosteum* (Hübichmann, *J.* 1856, 691; Enz, *C. C.* 1856, 393). Crystalline, insol. water, sol. alcohol and ether.

XYLOYL-BENZOIC ACID v. PHENYL XYLIL KETONE CARBOXYLIC ACID.

XYLOYL-FORMIC ACID v. XYLIL-GLYOXALIC ACID.

xy-DIXYLYL C_8H_8 , i.e.

[4:1:3] $C_6H_4Me_2$, $C_6H_4Me_3$ [3:4:1]. [125°]. Prepared by distilling mercury di-p-xylyl (Jacobsen, *B.* 14, 2112). Long needles (from alcohol).

Dixyl. (390°–395°). Formed from bromo- (7)-xylene and Na (Pittig, *A.* 147, 33). Liquid.

Di-xylyl (so-called). (295°) (Oliveri, G. 12, 158). Is got by warming commercial xylene with H_2SO_4 but never from xylene which has been made from xylene sulphonic acid. Hence it is probably not a benzene derivative (Armstrong, C. J. 45, 150). It is a colourless, fluorescent liquid, smelling like copaiba balsam.

XYLYL-ACETAMIDE v. *Acetyl derivative of Xylidine and Amide of XYLYL-ACETIC ACID.*

XYLYL-ACETIC ACID

[1:3:4] $\text{C}_6\text{H}_4\text{Me}_2\text{CH}_2\text{CO}_2\text{H}$. [102°]. Formed from its amide, which is got by the action of yellow ammonium sulphide on xylyl methyl ketone (Willgerodt, B. 21, 534). Slender needles.

Amide $\text{C}_6\text{H}_4\text{Me}_2\text{CH}_2\text{CONH}_2$. [183°].

Reference.—OXYXYLYL-ACETIC ACID.

XYLYL ALCOHOL is TOLYL-CARBINOL.

XYLYL-AMIDO-ACETIC ACID $\text{C}_6\text{H}_4\text{Me}_2\text{CH}_2\text{NO}_2$, i.e.

[1:3:4] $\text{C}_6\text{H}_4\text{Me}_2\text{NHCH}_2\text{CO}_2\text{H}$. [134°]. Formed by boiling *m*-xylidine (2 mols.) with water and chloro-acetic acid (1 mol.) (Ehrlich, B. 16, 205). Prisms (from dilute alcohol). Insol. water, v. sol. acids.

Xylide $\text{C}_6\text{H}_4\text{NHCH}_2\text{CO}_2\text{NHC}_6\text{H}_5$. [128°]. Formed by boiling xylidine (2 mols.) with chloro-acetic ether (1 mol.). Thick needles (from alcohol), insol. water and HClAq .

XYLYL-AMIDO-CROTONIC ETHER

[1:3:4] $\text{C}_6\text{H}_4\text{Me}_2\text{NH.CMe:CH.CO}_2\text{Et}$. Formed from *m*-xylidine and acetoacetic ether (Conrad, A. Limpach, B. 21, 526). Decomposed on heating into (Py. 1, 3; B. 2, 4)-oxy-tri-methyl-quinoline, di-xylyl-urea, and alcohol.

XYLYL-AMIDO-ETHYL-PHTHALIMIDE

[1:3:4] $\text{C}_6\text{H}_4\text{Me}_2\text{NH.C}_6\text{H}_4\text{N:C}_6\text{H}_4\text{O}_2$. [123°]. Formed by heating bromo-ethyl-phthalimid with *m*-xylidine at 140° (Newman, B. 21, 2197). Small needles, v. e. sol. benzene, al. sol. cold alcohol.

DI-*m*-XYLYL-DI-AMIDO-GLAZTHIOLE

$\text{C}_6\text{H}_4\text{N}_2\text{S}$ i.e. $\text{S} < \begin{matrix} \text{C}(\text{NHCH}_2)_2\text{N} \\ \text{C}(\text{NHCH}_2)_2\text{N} \end{matrix}$ [79°]. Formed by oxidising (1,3,4)-xylyl-thio-urea with aqueous H_2O_2 (Hector, B. 23, 368). Insol. water. Forms a very soluble hydrochloride.— $\text{B}^+\text{H.PtCl}_4$. Decomposes at 214°–217°.— B^+AgNO_3 . Explodes on heating. Blackened by sunlight.— $\text{B}^+\text{C}_6\text{H}_5\text{N}_3\text{O}$. [218°]. Yellow crystals, v. sol. alcohol. Cyanogen passed into its alcoholic solutions forms $\text{C}_6\text{H}_4\text{N}_2\text{SCy}$, [103°].

Acetyl derivative $\text{C}_6\text{H}_4\text{AcN}_2\text{S}$. Needles. *Benzoyl derivative* $\text{C}_6\text{H}_4\text{BzN}_2\text{S}$. [212°]. *Nitrosamine* $\text{C}_6\text{H}_4(\text{NO})\text{N}_2\text{S}$. [146°].

XYLYLAMINE v. *XYLIDINE* and *METXYL-BENZYL-AMINE*.

Di-*o*-xylyl-amine $(\text{C}_6\text{H}_4)_2\text{NH}$. (338°–345°). Formed, together with xylidine, by heating (1,3,4)-xylene with ammonio-zinc bromide and NH_4Br at 300° (Müller, B. 20, 1049). Liquid, solidified at a very low temperature.

Di-*m*-xylyl-amine. (305°–310°). Formed in like manner from *m*-xylidine. Oil.

Di-xylyl-amine. [162°]. Formed, together with a liquid isomeride, by heating xylidine with its hydrochloride (Girard, A. Vogt).

XYLYL-BENZYL-AMINE $\text{C}_6\text{H}_4\text{N}_2$, i.e. $\begin{matrix} \text{C}_6\text{H}_4\text{Me}_2\text{NHCH}_2\text{Ph} \\ \text{C}_6\text{H}_4\text{Me}_2\text{NHCH}_2\text{Ph} \end{matrix}$. (c. 205° at 15 mm.). Formed by heating *m*-xylidine with benzyl chloride at 160° (Joblin-Gobner, B. 18, 6, 21). Yellowish oil, sol. alcohol and benzene.

***p*-Xylyl-benzyl-amine**

[1:4:2] $\text{C}_6\text{H}_4\text{Me}_2\text{NHCH}_2\text{Ph}$. (322°) (Pflug, A. 256, 168).

***o*-XYLYL BENZYL KETONE** $\text{C}_6\text{H}_4\text{O}$ i.e. $\text{C}_6\text{H}_4\text{Me}_2\text{COCH}_2\text{Ph}$. [95°]. (310°–220° at 25 mm.). Formed from *o*-xylene, phenyl-acetic chloride, and AlCl_3 (Wege, B. 24, 3540). Plates, sol. alcohol, v. sol. ether. Yields a crystalline oxim.— NaOEt and benzyl chloride yield $\text{C}_6\text{H}_4\text{Me}_2\text{COCH}(\text{CH}_2\text{Ph})\text{Ph}$ [75°].

***m*-Xylyl benzyl ketone**

[1:3:4] $\text{C}_6\text{H}_4\text{Me}_2\text{COCH}_2\text{Ph}$. (350°). Formed, together with a smaller quantity of an isomeride [93°], by the action of AlCl_3 on a mixture of *m*-xylene and phenyl-acetic chloride (Sillischer, B. 15, 1681). Yields $\text{C}_6\text{H}_4\text{Me}_2(\text{CO}_2\text{H})_2$ [3:4:1] on oxidation. NaOEt and benzyl chloride form oily $\text{C}_6\text{H}_4\text{Me}_2\text{COCHPhCH}_2\text{Ph}$ (365°–375°).

***p*-Xylyl benzyl ketone** $\text{C}_6\text{H}_4\text{COCH}_2\text{Ph}$. (220°–230° at 26 mm.). Formed in like manner from *p*-xylene (Wege). Yields an oxim [99°] and a phenyl-hydrazone [96°]. NaOEt and benzyl chloride yield $\text{C}_6\text{H}_4\text{COCHPhCH}_2\text{Ph}$ [60–5°].

***m*-XYLYL-BENZYL-THIO-UREA**

$\text{C}_6\text{H}_4\text{NHCS.NHCH}_2\text{Ph}$. [85°]. Formed from benzyl-thiocarbimide and *m*-xylidine in alcohol (Dixon, C. J. 59, 558). Monoclinic prisms, v. sol. boiling alcohol and chloroform.

XYLYL BROMIDE v. *BROMO-XYLENE*.

XYLYL-*tert*-BUTANE $\text{C}_6\text{H}_4\text{Me}_2\text{CMe}_2$. [201°].

Formed from *m*-xylene, isobutyl bromide, and AlCl_3 (Baur, B. 24, 2840). Got also from isobutyl alcohol, *m*-xylene, and H_2SO_4 or ZnCl_2 (Nöbling, B. 25, 791). Oil, yields mesitylenic and trimetic acids on oxidation.

XYLYL-BUTYL ALCOHOL

[2:3:1] $\text{C}_6\text{H}_4\text{Me}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$. (above 270°). Got by reducing xylyl propyl ketone with zinc-dust and KOHAlq , or with sodium-amalgam (Claus, J. pr. [2] 46, 474). Oil, v. sol. alcohol and ether. Tri-xylyl-butyl alcohol $(\text{C}_6\text{H}_4)_3\text{CMe}_2\text{OH}$. (above 300°). Formed from *m*-xylene, tri-chloro-*tert*-butyl alcohol, and AlCl_3 (Willgerodt & Genieser, J. pr. [2] 37, 861). Oil, smelling like mushrooms.

***m*-XYLYL-*n*-BUTYRIC ACID**

[1:3:4] $\text{C}_6\text{H}_4\text{Me}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$. [70°]. Formed by saponifying the amide (Claus, J. pr. [2] 46, 476). Needles, v. sol. hot water. May be sublimed.— BaA , 4aq.— CaA , 4aq. Prisms, v. sol. water and alcohol.

Amide $\text{C}_6\text{H}_4\text{Me}_2\text{CH}_2\text{CH}_2\text{CONH}_2$. [124°]. Got by heating xylyl propyl ketone with S and ammonium sulphide in sealed tubes at 250°. Flat silky needles. May be sublimed.

***p*-Xylyl-*n*-butyric acid**

[1:4:2] $\text{C}_6\text{H}_4\text{Me}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$. [70°]. Needles, sl. sol. cold water.— BaA , 4aq.— CaA , 4aq. Needles, sol. water and alcohol.

Amide $\text{C}_6\text{H}_4\text{Me}_2\text{CH}_2\text{CH}_2\text{CONH}_2$. [125°]. Formed from *p*-xylyl propyl ketone (C). Flat needles, v. sol. hot water.

***m*-Xylyl-isobutyric acid**

[1:3:4] $\text{C}_6\text{H}_4\text{Me}_2\text{CH}_2\text{CHMeCO}_2\text{H}$. [70°]. Flat pearly needles, sol. hot water, alcohol, and ether. May be sublimed.

Amide $\text{C}_6\text{H}_4\text{Me}_2\text{CH}_2\text{CHMeCONH}_2$. [120°]. Got by heating xylyl isopropyl ketone with S and ammonium sulphide at 235° (Claus, J. pr. [2] 46, 483). Needles, sol. hot water.

XYLYL-CARBAMIC ACID

[1:3:4] $C_6H_4Me_2.NH.CO_2H$. *Ethyl ether EtA*. [58°]. Formed from *m*-xylidine and chloroformic ether (Hofmann, B. 3, 657; Frenzel, C. C. 1888, 1861). Needles.

Xylyl-carbamic acid

[1:3:5] $C_6H_4Me_2.NH.CO_2H$. *Ethyl ether EtA*. [77-5°] (Frenzel).

DI-*p*-XYLYL-CARBINOL

[(2:5:1) $C_6H_4Me_2.CH_2OH$. [181°]. Formed by reducing di-*p*-xylid ketone with zinc-dust and KOH (Elbs, J. pr. [2] 85, 484; B. 19, 408). White needles (from alcohol), nearly insol. Aq.

XYLYL CYANATE [1:3:4] $C_6H_4Me_2.N.CO$. [205°] (Frenzel, C. C. 1888, 1861).

Xylylcyanate [1:3:5] $C_6H_4Me_2.N.CO$. (208-5°).

XYLYL CYANURATE

[1:3:4] $(C_6H_4Me_2)_3N_3C_3O_3$. [162°] (Frenzel, C. C. 1888, 1861).

XYLYLENE ALCOHOL v. DI-OXY-XYLYLENE.

XYLYLENE-DI-ALLYL-DI-THIO-DI-UREA $(CH_2)_2C_6H_4(NH.CS.NH.C_2H_5)_2$. [1:4:2:6]. [112-5°]. Made from *p*-xylene diamine and allyl thiocarbimide (Lellmann, A. 228, 252). Needles (from alcohol). Not decomposed on melting.

***m*-XYLYLENE-*m*-DIAMINE**

$C_6H_4(CH_3)_2(NH_2)_2$. [1:3:4:6]. ***m*-Di-amido-*m*-xylene** [105°]. Formed by reduction of nitro-xylidine [128°] or of di-nitro-xylene [98°] (Fittig, A. 147, 18; Grevingk, B. 17, 2426; Witt, B. 21, 2419). White crystals. Sublimable. Does not yield a aurhodine on boiling with nitroso-dimethyl-aniline, NaOAc, and HOAc. — $B''HCl$. — $B''H_2PtCl_6$. — $B''H_2SO_4$. Crystalline, v. sq. Aq.

***m*-Xylylene-*o*-diamine**

$C_6H_4Me_2(NH_2)_2$. [1:3:5:6] [78-5°]. Formed by reduction of [2:4:1] $C_6H_4Me_2.N_2$, $C_6H_4Me_2.NH_2$ [1:3:5:6] (Nölting a. Forel, B. 18, 2688) and also by the action of tin and HClAq on di-bromo-di-nitro-xylene [191°] (Jacobsen, B. 21, 2821), and on (5,1,3,6)-nitro-xylidine (Hofmann, B. 9, 1298). Plates (from water), sl. sol. cold benzene, sol. ether.

***m*-Xylylene-*m*-diamine**

$C_6H_4Me_2(NH_2)_2$. [1:3:4:2]. [64°]. Formed by reduction of nitro-xylidine [78°] or of di-nitro-*m*-xylene [82°] (Grevingk, B. 17, 2426). White needles. Gives a Bismarck brown with nitrous acid and a chrysoidine with diazobenzene.

***p*-Xylylene-*o*-diamine**

$C_6H_4Me_2(NH_2)_2$. [1:4:2:3]. [75°]. Formed by reduction of *o*-di-nitro-*p*-xylene (Lellmann, A. 228, 251; Nölting, B. 19, 145). White needles (by sublimation). Gives a deep-red colour with $FeCl_3$.

***p*-Xylylene-*m*-diamine**

$C_6H_4Me_2(NH_2)_2$. [1:4:2:6]. [102°]. Formed by reducing (2,6,1,4)-di-nitro-xylene (L. & N.). Needles (by sublimation). Behaves like *m*-diamine.

***p*-Xylylene-*p*-diamine**

$C_6H_4Me_2(NH_2)_2$. [1:4:2:5]. [142°] (S.); [147°] (N. a. F.); [150°] (N.). **Formation**.—1. By reduction of xylene-azoxyldine (amido-azo-xylene) [2:5:1] $C_6H_4Me_2.N_2$, $C_6H_4Me_2.NH_2$ [1:2:5:4] by zinc and HClAq (Nietzki, B. 18, 471; Nölting a. Forel, B. 18, 2685).—2. By reduction of nitro-*p*-xylidine [142°] (Nölting, Witt, a. Forel, B. 18, 2666; von Kostanecki, B. 19, 2818; Marekwald, B. 23, 1021).—3. By reduction of the di-oxim of

p-xyloquinone $C_6H_4Me_2(NO_2)_2$, with tin and HCl (Sutkowski, B. 30, 979).

Properties.—Colourless needles, sol. hot water and alcohol, m. sol. benzene and ether. Yields xylequinone [128°] on oxidation. Not oxidised by exposure to air. May be sublimed.

Salts.— $B''HCl$. Colourless leaflets. — $B''H_2SO_4$. Crystalline meal.

***o*-Xylylene-*exo*-diamine**

[1:2] $C_6H_4(CH_2NH_2)_2$. Formed by heating the phthalimide $C_6H_4(CH_2N:O_2C_2H_5)_2$, with conc. HClAq at 200° (Strassmann, B. 21, 579). Alkaline liquid, smelling strongly like ammonia. Absorbs CO_2 . Gives with $FeCl_3$ a pp. of yellowish-red needles. — $B''HCl$. — $B''H_2AuCl_4$. Yellow plates. — $B''H_2C_2H_4N_2O$. Yellow needles, decomposing above 170° without melting.

Acetyl derivative $C_6H_4Ac_2N_2$. [146°].

Benzoyl derivative $C_6H_4Bz_2N_2$. [168°].

***m*-Xylylene-*exo*-diamine**

[1:3] $C_6H_4(CH_2NH_2)_2$. [247°]. Formed by the action of conc. hydrochloric acid at 220° on the $C_6H_4(CH_2N:C_2H_5O_2)$ [237°], which is got by heating potassium phthalimide with di-*o*-bromoxylene (Brömme, B. 21, 2705). Liquid, sol. water, miscible with alcohol and ether. Absorbs CO_2 . — $B''HCl$. Needles (from water). — $B''H_2H_2PtCl_6$. — $B''H_2C_2H_4N_2O$. Yellow spangles, decomposing at 187°.

Acetyl derivative $C_6H_4(CH_2NHAc)_2$.

[119°]. Crystalline mass, v. sol. hot water.

Reference.—NITRO-XYLYLENE-DIAMINE.

XYLYLENE-BENZENYL-AMIDINE v. BENZ-**ENYL-XYLYLENE-DIAMINE.****XYLYLENE BROMIDE v. DI-BROMO-XYLYLENE.****XYLYLENE-CHLORO-MALONIC ETHER v.****CHLORO-XYLYLENE-MALONIC ETHER.**

Xylylene-*exo*-di-chloro-malonic ether v. Di-

CHLORO-PHENYLENE-DI-METHYL-DI-MALONIC ETHER.**XYLYLENE-ETHENYL-AMIDINE** $C_6H_4H_2N_2$

i.e. $CMe < \text{N} > C_6H_4Me_2$. Formed by reducing

$C_6H_4Me_2(NO_2)(NHAO)$ [1:3:5:4] with tin and HCl (Hobrecker, B. 5, 922). Resinous mass. — $B''HCl$. Large needles. — $B''H_2PtCl_6$. — $B''HNO_3$. Long needles.

XYLYLENE IODIDE v. DI-iodo-XYLYLENE.**XYLYLENE-DI-MALONIC ACID v. PHENYL-****ENE-DI-METHYL-DI-MALONIC ACID.*****o*-XYLYLENE SULPHIDE** C_6H_4S i.e.

$C_6H_4 < \text{CH}_2 > S$. [a. 0°]. Formed by heating di-*o*-bromo-*o*-xylene with K_2S (Leser, B. 17, 1824; Hjelt, B. 22, 2904). Oil, smelling like mercaptan. Very unstable, quickly turning into a black resin. — $B''HgCl_2$. Long needles.

Methylo-iodide $B''MeI$. [155°].

Di-xylylene disulphide

[1:3:4:5] $C_6H_4Me_2S_2$, $C_6H_4Me_2$ [5:4:3:1]. [118°]. Formed by heating xylene-diazosulphide at 200°-250° (Jacobsen a. Ney, B. 22, 911). Conc. H_2SO_4 forms a blue liquid, remaining blue on dilution.

***u*-DI-XYLYL-ETHANE** C_6H_4 i.e.

$CH_2CH(OH)_2$ (314°). SG_{20}^{20} 966. Formed from ethylidene chloride, *m*-xylene, and $AlCl_3$ (Apschütz, B. 18, 865; A. 285, 826). Oil.

Reference.—CHLORO-DI-XYLYL-ETHANE.**DI-XYLYL-ETHYLENE** C_6H_4 i.e.

$C_6H_4Me_2CH:CHC_6H_4Me_2$. **Tetra-methyl-stilbene**. [106°]. ϵ (325°-340°). Formed by distilling

$\text{O}_2\text{H}_2\text{Me}_2\text{CH}_2\text{OH}\cdot\text{Cl}$, which is got from di-chloro-di-ethyl oxide, *m*-xylene, and H_2SO_4 (Hepp, *B.* 7, 1416). Spangles (from alcohol), sol. ether and CS_2 . Unites with bromine. Oxidised by dilute HNO_3 to (1,3,4)-di-methyl-benzoic acid [129°].

Di-xylyl-ethylene $\text{C}_6\text{H}_4\text{Me}_2\text{CH}:\text{CH}\cdot\text{C}_6\text{H}_4\text{Me}_2$. [157°]. Formed in like manner from *p*-xylene. Plates (from alcohol). Less soluble than the preceding isomeride.

Tetra-xylyl-ethylene $(\text{C}_6\text{H}_4\text{Me}_2)_2\text{C}:\text{C}(\text{C}_6\text{H}_4\text{Me}_2)_2$. [245°]. Formed from xylene, CHCl_3 , and AlCl_3 (Schwarz, *B.* 14, 1528). Yellow plates.

***m*-XYLYL-ETHYLENE-DIAMINE** $\text{C}_6\text{H}_4\text{Me}_2\text{NH}\cdot\text{C}_6\text{H}_4\text{NH}_2$. (274°). Formed from *m*-xylyl-amido-ethyl-β-thalimide and HCl (Newman, *B.* 24, 2197).— B^+HCl . [173°].— $\text{B}^+\text{H}_2\text{PtCl}_6$.— $\text{B}^+\text{C}_6\text{H}_5\text{N}_3\text{O}$. [141°]. Reddish-yellow needles, v. s. sol. alcohol.

DI-*m*-XYLYL-ETHYLENE DIKETONE $\text{C}_6\text{H}_4(\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}_2)_2$. [129°]. Formed from *m*-xylene, succinyl chloride, AlCl_3 and CS_2 (Claus, *B.* 20, 1375). Needles, insol. water, v. sol. alcohol and ether. Dilute HNO_3 oxidises it to (1,3,4)-di-methyl-benzoic acid.

Oxim $\text{C}_6\text{H}_4(\text{C}(\text{NOH})\cdot\text{C}_6\text{H}_4)_2$. [140°]. **Phenyl-hydrazide** $\text{C}_6\text{H}_4(\text{N}(\text{HPh})\cdot\text{C}_6\text{H}_4)_2$. [189°]. Crystals.

Di-*p*-xylyl-ethylene diketone $\text{C}_6\text{H}_4(\text{CO}\cdot\text{C}_6\text{H}_4\text{Me}_2)_2$. [123°]. Formed from *p*-xylene, succinyl chloride, AlCl_3 , and CS_2 (Claus). Needles.

***m*-XYLYL ETHYL KETONE** [1:3:4] $\text{C}_6\text{H}_4\text{Me}_2\text{CO}\cdot\text{C}_6\text{H}_4$. (239°). Light oil, with aromatic odour, not solid at -10° (Claus, *J. pr.* [2] 43, 140). Yields (1,3,4)-di-methyl-benzoic acid on oxidation.

Phenyl-hydrazide [126°]. Plates, v. sol. hot water, alcohol, and ether.

***p*-Xylyl ethyl ketone** [4:1:2] $\text{C}_6\text{H}_4\text{Me}_2\text{CO}\cdot\text{C}_6\text{H}_4$. (238° uncor.). Formed from *p*-xylene, AlCl_3 , and propionyl chloride (Claus a. Fickert, *B.* 19, 3182). Oil. Oxidised by KMnO_4 to $\text{C}_6\text{H}_4\text{Me}_2\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{H}$ [132°] and some (4,1,2)-di-methyl-benzoic acid.

***m*-XYLYL ETHYL KETONE CARBOXYLIC ACID** [4:2:1] $\text{C}_6\text{H}_4\text{Me}_2\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. [108°].

Di-methyl-benzoyl-propionic acid. Formed from *m*-xylene, succinyl chloride, AlCl_3 , and CS_2 (Claus, *B.* 20, 1376). Needles, v. sol. hot water, insol. cold.— NH_4A^+ .— KA^+ 4aq. V. sol. water.— NaA^+ 4aq. Needles.— BaA^+ 3aq. Needles.— PbA^+ : white pp.— AgA^+ : white crystalline pp.

***p*-Xylyl ethyl ketone carboxylic acid** [4:1:2] $\text{C}_6\text{H}_4\text{Me}_2\text{CO}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. [84°]. Formed from *p*-xylene in like manner (C_6H_4). Colourless needles.

XYLYL-DI-ETHYL-PHOSPHINE $\text{C}_6\text{H}_4\text{Me}_2\text{P}(\text{Et})_2$. (260°). Formed by the action of ZnEt_2 on $\text{C}_6\text{H}_4\text{Me}_2\text{P}\cdot\text{Cl}_2$ (Czimatia, *B.* 15, 2016). Thick, colourless oil. Yields B^+MeI [90°], $\text{B}^+\text{MePtCl}_6$ [202°], and B^+EtI [186°].

***m*-XYLYL-GLYOXALINE** $\text{C}_6\text{H}_4\text{N}(\text{CH}:\text{CH}\cdot\text{CH}:\text{N})_2$. [35°]. (279°). Formed by the action of HNO_3 on $\text{C}_6\text{H}_4\text{N}(\text{CH}:\text{CH}\cdot\text{CH}:\text{N})_2$ [192°], which is got by the action of HCl on the product of the action of amido-acetal on *m*-xylyl-thio-urea (Marck-

wald, *B.* 25, 2368). Sl. sol. water.—Aurochloride [165°].—Picrate. [159°]. Yellow needles, m. sol. chloroform.

***o*-XYLYL-GLYOXYLIC ACID**

[4:3:1] $\text{C}_6\text{H}_4\text{Me}_2\text{CO}\cdot\text{CO}_2\text{H}$. [92°]. Formed by oxidising *o*-xylyl methyl ketone with alkaline K_2FeCy , (Buohka a. Irish, *B.* 20, 1766).— BaA^+ .

***m*-Xylyl-glyoxylic acid**

[4:2:1] $\text{C}_6\text{H}_4\text{Me}_2\text{CO}\cdot\text{CO}_2\text{H}$. [54°]. Formed by oxidising *m*-xylyl methyl ketone with KMnO_4 (Claus, *B.* 19, 231; *J. pr.* [2] 43, 149). Flat prisms. Yields (4,2,1) di-methyl-benzoic acid on boiling with dilute HNQ_3 . Gives rise to $\text{C}_6\text{H}_4\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ [119°] on reduction.— CaA^+ 2aq. Needles.— BaA^+ 2aq.— AgA^+ . Needles, sol. hot water.

***p*-Xylyl-glyoxylic acid**

[5:2:1] $\text{C}_6\text{H}_4\text{Me}_2\text{CO}\cdot\text{CO}_2\text{H}$. [70°–80°]. Formed by oxidation of *p*-xylyl methyl ketone by aqueous KMnO_4 (Claus a. Wollner, *B.* 18, 2859). Crystalline, v. sol. alcohol, ether, and HOAc , v. sl. sol. water. Splits up above 200° into CO_2 and di-methyl-benzoic aldehyde. Oxidised by HNO_3 to $\text{C}_6\text{H}_4\text{Me}_2\text{CO}_2\cdot\text{H}\cdot\text{AcO}$ and NaOAc yield di-methyl-cinnamic acid.— BaA^+ 6aq.: small felted needles.— CaA^+ 3aq.— AgA^+ : crystalline pp.

Ethyl ether EtA. Oil.

XYLYL GLYOXYLIC ALDEHYDE

[1:3:4] $\text{C}_6\text{H}_4\text{Me}_2\text{CO}\cdot\text{CHO}$. **Oxim** [95°]. Formed from xylyl methyl ketone, NaOEt , and $\text{C}_6\text{H}_5\text{NO}_2$ (Söderbaum, *B.* 25, 3163). Needles (from benzene-ligroin). Acetic anhydride gives the acetyl derivatives of the *syn*-oxim $\text{C}_6\text{H}_4\text{Me}_2\text{CO}\cdot\text{CH}:\text{NOAc}$ [54°] decomposed by alkalis with formation of $\text{C}_6\text{H}_4\text{Me}_2\text{CO}\cdot\text{H}$ [126°] and by hot Ac_2O yielding $\text{C}_6\text{H}_4\text{Me}_2\text{CO}\cdot\text{CN}$ [47°]. AcCl converts the oxim into $\text{C}_6\text{H}_4\text{Me}_2\text{C}(\text{OH})\cdot\text{CH}:\text{NOAc}$ [142°], whence cold NaOH forms $\text{C}_6\text{H}_4\text{Me}_2\text{CH}(\text{OH})\cdot\text{CO}_2\text{H}$ [103°], while NaOHAq at 50° forms 'xylyl formoin' $\text{C}_6\text{H}_4\text{CO}\cdot\text{CH}(\text{OH})\cdot\text{CO}\cdot\text{CO}_2\text{H}$, [155°].

DI-XYLYL-GUANIDINE

$\text{HN}\cdot\text{C}(\text{NH}\cdot\text{C}_6\text{H}_4)_2$. [158°]. Formed by the action of PbO and alcoholic ammonia on di-xylyl-thio-urea (Hofmann, *B.* 9, 1295). Needles, (from alcohol).

XYLYL-HYDRAZINE

[4:2:1] $\text{C}_6\text{H}_4\text{Me}_2\text{NH}\cdot\text{NH}_2$. [85°]. Formed from xylidine by diazotisation followed by reduction with Na_2SO_3 , the resulting $\text{C}_6\text{H}_4\text{Me}_2\text{NH}_2\cdot\text{SO}_3\text{Na}$ 3aq being then treated with zinc-dust and HOAc (Klauber, *M.* 11, 282). Pale-yellow needles, v. sl. sol. water, v. sol. alcohol. Reduces Fehling's solution on warming. On heating with aceto-acetic ether it yields a crystalline body [203°] reduced, in alcoholic solution by Na to oxy-xylyl-methyl-pyrazole.

Salt:— $\text{C}^+\text{HCl}^-\cdot 2\text{H}_2\text{O}$. [183°]. Small needles.

Di-*o*-xylyl-hydrazine

[3:2:1] $\text{C}_6\text{H}_4\text{Me}_2\text{NH}\cdot\text{NH}\cdot\text{C}_6\text{H}_4\text{Me}_2$ [1:2:3]. [141°]. ***o*-Hydrazo-*o*-xylene**. Got by heating nitro-*o*-xylene (20 g.) with NaOH (20 g.) alcohol (100 c.c.) and zinc-dust (25 g.) and reducing the product with alcoholic ammonium sulphide (Nöling a. Stricker, *Bl.* [2] 50, 613). White needles, sol. alcohol and ether. Easily oxidised by air.

***u*-Di-*o*-xylyl-hydrazine**

$\text{N}_2\text{H}_4(\text{C}_6\text{H}_4\text{Me}_2)_2$ [1:3:4]. [107°]. Formed by reducing nitro-*o*-xylene with sodium-amalgam (N. a. S.). Yellowish white needles, sol. alcohol.

Di-*m*-xylyl-hydrazine
 $N_2H_4(C_6H_4Me_2)_{1:2:5}$. [125°]. Obtained from *s*-nitro-*m*-xylene (N. a. S.). Needles, easily oxidised by air.

***o*-Di-*m*-xylyl-hydrazine**
 $N_2H_4(C_6H_4Me_2)_{1:2:4}$. [122°]. Gp't by warming nitro-*m*-xylene (80 g.) with NaOH (80 g.), zinc-dust (40 g.), and alcohol (250 c.c.) and treating the xylene-azo-xylene so obtained with alcoholic ammonia and H_2S (N. a. S.). White needles, sol. alcohol and ether.

Di-*p*-xylyl-hydrazine
 $N_2H_4(C_6H_4Me_2)_{1:2:5}$. [145°]. Formed from nitro-*p*-xylene (N. a. S.). Needles, not affected by air.

XYLYLIC ACID *v.* DI-METHYL-BENZOIC ACID.

***o*-Xylylic acid** *v.* TOLYL-ACETIC ACID.

***p*-XYLYLIDENE-DI-IMINE**

$C_6H_4(CH.NH)_{1:4}$. Formed by the action of alcoholic NH_3 or dry NH_3 gas upon terephthalic aldehyde (Oppenheimer, B. 19, 576). Glassy brittle crystals. V. cl. sol. alcohol and ether.

DI-XYLYL-KETONE $CO(C_6H_4Me_2)_2$ (c. 340°). Obtained from (*m*?)-xylene, $COCl_2$, and $AlCl_3$ (Ador a. Rilliet, B. 11, 399). Liquid, not solid at -60°. Split up by long boiling into H_2O and C_6H_4 .

Di-*p*-xylyl ketone

[2:5:1] $C_6H_4Me_2.CO.C_6H_4Me_2$ [1:2:5]. (327° uncor.). Formed from *p*-xylene, CS_2 , and $COCl_2$ in closed vessels; the yield being 55 p.c. (Elbs, J. pr. [2] 35, 481). Oil. Quickly decomposed by distillation into H_2O and (*B*. 2, 1'4')-tri-methyl-anthracene [227°]. Reduced by zinc-dust and alcoholic KOH to di-*p*-xylyl-carbinol [181°].

Di-xylyl-tetraz ketone

$C_6H_4.CO.CO.CO.CO.C_6H_4Me_2$ [4:3:1]. [180°]. Formed by the action of cold HNO_3 (S.G. 1:4) on $C_6H_4.CO.CH(OH).CO.CO.C_6H_4$ (Säderbaum, B. 25, 8475). Scarlet needles (from CS_2). On dissolving in $HOAc$ and ppg. by water it yields a dihydrate [100°] $C_6H_4O_2$.

XYLYL MERCAPTAN $C_6H_4Me_2.SH$. [214°]. S.G. 1:1.036. Got by treating xylene sulphonic chloride with Zn and dilute H_2SO_4 (Ysells, Z. 1865, 860), and also by heating xylyl ethyl xanthate with alcoholic potash (Leuckart, J. pr. [2] 41, 192). Liquid. — $Hg(E.C_6H_4)_2$. — $Pb(S.C_6H_4)_2$. Yellow powder.

TRI-*p*-XYLYL-METHANE $CH(C_6H_4Me_2)_3$. [188°]. (above 360°). From di-*p*-xylyl-carbinol, *p*-xylene, and H_2O by boiling for four hours (Elbs, J. pr. [2] 85, 484). Crystalline grains (from alcohol), v. sol. ether and benzene.

***o*-XYLYL METHYL KETONE**

[4:3:1] $C_6H_4Me_2.CO.CH_3$. [246°]. Formed from *o*-xylene, $AcCl$, and $AlCl_3$ (Ullas, B. 18, 1856; 19, 232; J. pr. 1890, 410). Oil, smelling like coumarin (Armstrong, C. J. 83, 81). Yields (4,3,1)-di-methyl-benzoic acid on oxidation. Conc'd $HClAq$ forms $C_6H_4O_2$ [114°]. P_2O_5 gives a body melting at 165°. Zinc-dust reduces the ketone to $C_6H_4.CH(OH).CH_3$ (257°).

Oxim $C_6H_4.(NOH).CH_3$. [85°]. Prisms (from dilute alcohol), converted by $AcCl$ into $C_6H_4.C(NOAc).CH_3$. [72°].

Phenyl-hydrazide. Colourless prisms.

***m*-Xylyl methyl ketone**

[4:2:1] $C_6H_4Me_2.CO.CH_3$. (228°). Formed from *m*-xylene, $AcCl$, and $AlCl_3$ (Claus, B. 19, 280).

Obtained also by boiling *m*-xylene with $HOAc$, $ZnCl_2$, and $POCl_3$ (Frey, J. pr. [2] 49, 120). Oil smelling like peppermint. Not condensed by $HClAq$. Yields $C_6H_4Br_2O$ [69°]. Reduction by HI yields $C_6H_4Me_2.CH_2.CH_3$ (184°) (Claus, J. pr. [2] 45, 830). HNO_3 gives $C_6H_4.N_2O_4$ [408°] (Claus, J. pr. [2] 41, 492).

***p*-Xylyl methyl ketone**

[5:2:1] $C_6H_4Me_2.CO.CH_3$. (225° uncor.). S.G. 1:2.9962. V.D. 4.93. Formed from *p*-xylene, $AcCl$, and $AlCl_3$ (Claus a. Wollner, B. 18, 1856). Oil, v. sol. alcohol and ether. Oxidised by hot aqueous $KMnO_4$ to *p*-xylyl-glyoxylic acid. Dilute HNO_3 forms di-methyl-benzoic and methyl phthalic acids.

Oxim $C_6H_4.(NOH).CH_3$. [58°].

***o*-XYLYL METHYL KETONE CARBOXYLIC ACID** *v.* METHYL-BENZOYL-ACETIC ACID.

XYLYL-DI-METHYL-PHOSPHINE

$C_6H_4Me_2.PMe_2$. (230°). Formed from $ZnMe_2$ and $C_6H_4Me_2.PCl_2$ (Czismatis, B. 15, 2016). Oil Unites with CS_2 , forming a compound [115°].

XYLYL-METHYL-THIOHYDANTOIN

[3:4] $C_6H_4Me_2.N < \begin{matrix} CO.CH_2 \\ CS.NH \end{matrix}$. [165°]. Formed from xylyl-thiocarbimide and alanine (Marckwald, B. 24, 3282). Needles, v. sol. alcohol.

XYLYL PENTADECYL KETONE

$C_6H_4Me_2.CO.C_{15}H_{31}$. [87°]. (269° at 15 mm.). Formed from *m*-xylene, palmityl chloride, and $AlCl_3$ (Krafft, B. 21, 2269). Small plates, yielding di-methyl-benzoic acid [126°] on oxidation.

XYLYL PHENYLAMYL KETONE

$C_6H_4Me_2.CO.CHPh.C_6H_5$. [91:5°]. Formed by Friedel and Craft's method (Wege, B. 24, 8541).

XYLYL-PHENYL- *v.* PHENYL-XYLYL-

TRI-XYLYL PHOSPHATE $PO(OC_6H_4Me_2)_3$.

The *o*- and *p*-compounds are formed by heating *o*- and *p*-xylene with $POCl_3$ (Kreyler, B. 18, 1702). They are oils, v. sol. ether, alcohol, and benzene.

***m*-XYLYL-PHTHALIDE**

$C_6H_4 \begin{matrix} \diagup CH(C_6H_4Me_2) \\ \diagdown CO \end{matrix} O$. [84°]. Got by heating $C_6H_4Me_2.CO.C_6H_4.CO.H$ with zinc and HCl (Greslay, A. 234, 237). Needles (from alcohol), sl. sol. benzene.

XYLYL-PROPIONIC ACID

[1:3:4] $C_6H_4Me_2.CH_2.CH_2.CO_2H$. [105°]. Formed by saponifying the amide. Silky needles, v. sol. hot water. — BaA , 6aq. Plates, m. sol. water. — CaA , 4aq. — AgA . White powder.

Acide $C_6H_4Me_2.C_6H_4.CO.NH_2$. [107°]. Got by heating the oxim of *m*-xylyl ethyl ketone with yellow ammonium sulphide under pressure (Claus, V. pr. [2] 46, 477). Needles, sol. hot water.

***m*-XYLYL PROPYL KETONE** C_6H_4O *is*.

[4:2:1] $C_6H_4Me_2.CO.Pr$. (251°). Formed from *m*-xylene, butyryl chloride and $AlCl_3$ (Claus, J. pr. [2] 46, 474). Oil, v. sol. alcohol and ether. Yields *m*-xylyl-glyoxylic acid [54°] on oxidation with $KMnO_4$.

Oxim. Crystals, v. e. sol. alcohol.

***p*-Xylyl propyl ketone** [5:2:1] $C_6H_4Me_2.CO.Pr$. (249°). Formed in like manner from *p*-xylene. Light oil.

Oxim [47°]. Colourless needles.

***o*-Xylyl isopropyl ketone**

[4:3:1] $C_6H_4Me_2.CO.Pr$. (258°). Oil, smelling like

terpentine (Claus, *J. pr.* [2] 46, 484). Yields di-methyl-benzole acid [163°] on oxidation.

Ozīm [68°]. Large prisms.

m-Xylyl isopropyl ketone [4:2:1] $C_8H_9Me.CO.Pr.$ (245°). Oil, yielding *m*-xylyl-glyoxylic acid on oxidation by $KMnO_4$.

Ozīm [97°]. Prisms (from alcohol).

Phényl-hydrasie [129°]. Crystals.

p-Xylyl isopropyl ketone

[8:2:1] $C_8H_9Me.CO.Pr.$ (240°). Formed from *p*-xylene, isobutyryl chloride, and $AlCl_3$ (Claus, *J. pr.* [2] 46, 484). Oil, smelling like mushrooms.

Ozīm [76°]. Plates and prisms.

TETRA-*o*-XYLYL SILICATE $Si(OC_8H_4Me)_4$. (c. 480°). Formed by heating *o*-xylene with $SiCl_4$, the yield being 85 p.c. of the theoretical amount (Hertkorn, *B.* 18, 1691). Large prisms.

Tetra-*m*-xylyl silicate $Si(OC_8H_4Me)_4$. (453°-457°). Formed, in like manner, from *m*-xylene. Oil.

***m*-XYLYL THIOCARBIMIDE** C_8H_4NS i.e. [4:2:1] $C_8H_4Me.N:CS$. Formed from di-xylyl-thio-urea and P_2O_5 (Hofmann, *B.* 9, 1295). Crystals. Converted by $PhOEt$ and $AlCl_3$ into $C_8H_4NH.CO.S.C_2H_5.OEt$ [140°] (Gattermann, *B.* 25, 3530).

XYLYL ETHYL DITHIOCARBONATE

$CS(OEt)_2.C_8H_4Me$. Formed from potassium

xanthate and *m*-diaz-xylylene chloride (Louchart, *J. pr.* [2] 41, 192). Oil, converted by heating with alcoholic potash into xylyl mercaptan (214°).

DI-XYLYL-THIO-UREA

$CS(NH.C_8H_4Me)_2$ [1:2:4]. [158°]. Formed by digesting xylydine with CS_2 , as long as H_2S escapes (Hofmann, *B.* 9, 1295). Crystals (from alcohol).

XYLYL-UREA $NH_2.CO.NHO.C_8H_4Me$ [1:2:4]. [186°]. Formed from crude xylydine sulphate and potassium cyanate (Genz, *B.* 8, 226). Needles (from alcohol).

s-Xylyl urea $NH_2.CO.NHO.C_8H_4Me$ [1:3:5]. [162°] (Frentzel, *C. C.* 1888, 1361).

Di-s-xylyl-urea $CO(NHO.C_8H_4Me)_2$ [1:3:5]. [275°] (F.); [251°] (G. a. C.). Formed from *s*-xylydine and $COCl_2$ (F.). Formed also from *m*-xylyl cyanate and xylydine (Gattermann a. Cantzler, *B.* 25, 1089). Needles.

Di-m-xylyl-urea $CO(NH.C_8H_4Me)_2$ [1:2:4]. [263°]. A product of the distillation of *m*-xylyl-amido-crotonic acid (Conrad a. Limpach, *B.* 21, 527). Sublimes when melting.

Di-xylyl-urea $CO(NHC_8H_4Me)_2$. Formed by heating urea (1 pt.) with crude xylydine (8 pts.). Felted needles (from hot alcohol), not melted at 250° (Genz, *B.* 3, 226).

Reference. — METHYL-BENZYL-UREA.

Y

YTTERBIUM. Yb. At. w. c. 173. This name is given to the metal, not yet isolated, of an earth separated by Marignac, in 1878, from crude erbia obtained from *gadolinite* or *euxenite*. The claim of ytterbia to rank as a definite homogeneous compound is not yet satisfactorily established.

The discovery of a new earth in a mineral from Ytterby in Sweden was announced in 1788 by Gadolin; in 1797 Ekeberg confirmed the discovery. The new earth was named *yttria*, and the mineral from which it was obtained was called *gadolinite*. Researches into the nature of yttria were conducted by Berzelius in 1819 (*v. Lehrbuch* [5th ed.] 2), Mosander in 1839 and 1843 (*J. pr.* 30, 27), Scheerer in 1849, Clève and others. In 1878 Marignac made a careful examination of erbia (*M. Ch.* [5] 14, 247); he fractionally decomposed erbium nitrate by heat, and obtained an earth which he called *ytterbia*. The erbia used by Marignac was pink, and gave, in solution, an absorption spectrum; the new earth was white and showed no absorption spectrum. Nilson (*B.* 12, 554; 13, 1439 [1879-89]) prepared ytterbia, but found a reacting weight for the earth different from that assigned to it by Marignac. By repeated fractional decomposition by heat of the nitrate of ytterbium, Nilson separated another earth which he called scandia (*cf.* Scandrium, this vol., p. 481). Nilson (*B.* 13, 1430) in 1879 made a fuller examination of ytterbia, and determined the at. w. of the metal of this earth, and the properties of several salts of the metal. In this memoir Nilson asserted

that erbia was separable into seven distinct earths: erbia proper, scandia, terbia, thulia, ytterbia, yttria, and Soret's X (afterwards called holmia). (*cf.* Erbium, vol. ii. p. 459; and METALS, RARE, vol. iii. p. 245).

Occurrence. — Along with erbia, scandia, yttria, &c., in very small quantities in a few rare Scandinavian minerals, chiefly in *gadolinite* and *euxenite*. Nilson (*l.c.*) obtained c. 20 g. ytterbia from 6-7 kilos. of the crude earths prepared from c. 15 kilos. *gadolinite*.

Preparation of ytterbia. — Nilson (*B.* 13, 1430) mixed finely powdered *euxenite* or *gadolinite*, c. 400 g. at a time, with four times its weight of $KHSO_4$, fused over a powerful burner, pulverised the fused mass, and thoroughly exhausted with cold water; he ppd. the aqueous solution by ammonia, washed the ppd. separated oxides, and dissolved in HNO_3 Aq; after boiling the solution for some time, and filtering, he ppd. by oxalic acid, washed the pp., dried it, and heated strongly until it was decomposed. The crude earths thus obtained were freed from K_2CO_3 by boiling with water, and were then dissolved in HNO_3 Aq; the solution was evaporated to dryness, and the residue was fused until red vapours began to come off. The reddish-yellow, opaque solid was then treated with boiling water, whereby a reddish-yellow pp. was formed, which was filtered off by means of a suction-pump. (This pp. contained oxide of Th, along with oxides of Ce, Fe, and U.) The reddish filtrate was evaporated to dryness, and the solid nitrates thus obtained were partly decomposed by heating, the soluble

(undecomposed) portion removed by solution in water, the residue dissolved in HNO_3Aq , the solution evaporated to dryness, the residue partly decomposed by heating, the undecomposed nitrates were removed by washing with water, the residue was dissolved in HNO_3Aq , and so on. After thirty repetitions of this process a solution was obtained that showed merely a trace of red colour after thirty-five repetitions the solution was quite colourless, and showed only two faint absorption bands, one in the green and the other in the red; after forty repetitions a solution was obtained which gave only the red band; and when the process of partial decomposition by heat had been repeated sixty-eight times a solution in HNO_3Aq was obtained which showed no trace of an absorption spectrum. This solution was saturated with H_2S , the small yellowish-brown pp. of PbS was filtered off, the filtrate was ppd. by pure oxalic acid, the pp. was washed, dried, and decomposed by heating strongly, and pure ytterbia was thus obtained. For a modification of this method of separating ytterbia from accompanying earths *v. Auer von Welsbach (M. 4, 630)*.

Atomic weight of ytterbium.—The metal has not been isolated; the at. w. was determined by Nilson (*B. 13, 1433*) by dissolving pure Yb_2O_3 (*v. supra*) in HNO_3Aq , adding a suitable quantity of $\text{H}_2\text{SO}_4\text{Aq}$, evaporating on a water-bath to drive off HNO_3 , then on a sand-bath, and finally over a flame until all free H_2SO_4 was removed, weighing the $\text{Yb}_2(\text{SO}_4)_3$ thus obtained, and analysing it. Nilson dissolved pure Yb_2O_3 in HNO_3Aq , evaporated to dryness, partially decomposed the nitrate by heat, treated with water, &c., as described *supra*, and in this way obtained seven fractions, each of which was converted into sulphate. The results are presented in the following table:—

Weight of Yb_2O_3 taken	Weight of sulphate formed	Pctge. composition of sulphate		Atomic w. of Yb.
		Yb_2O_3	SO_3	
1.0063	1.6186	62.171	37.829	173.21
1.0189	1.6314	62.149	37.851	173.03
8509	1.3690	62.155	37.845	173.08
7371	1.1861	62.145	37.855	173.00
1.0005	1.6099	62.147	37.853	173.01
8090	2.3022	62.126	37.874	173.84
1.0059	1.6189	62.134	37.866	172.91
Mean		62.147	37.853	173.01

Chemical relations of ytterbium.—If Yb is really a homogeneous substance, it must be placed in Series 10 of Group III. in the periodic classification of the elements. This group contains the following elements:—

<i>Even series</i> —				
2	4	6	8	10
B (11)	Sc (14)	Y (89)	La (139)	Yb (173)
<i>Odd series</i> —				
3	5	7	9	11
Al (27)	Ga (70)	In (114)	—	Tl (204)

A comparison of the position of Yb with the positions of elements placed in Series 10 (*v. table on p. 811 of vol. iii.*) shows that Yb

ought to be decidedly more metallic than B, and somewhat more metallic than Al, Ga, or In; the data, however, are too meagre to allow a detailed comparison to be made. Little is known of the properties of compounds of Yb; but what is known broadly confirms the conclusions drawn from the position of the element in the periodic scheme of classification (*cf. EARTHS, METALS OF THE*, vol. ii. p. 424).

Ytterbium oxide Yb_2O_3 . (*Ytterbia*.) A very heavy, white, infusible powder; slowly acted on by acids when cold or gently warmed, but readily dissolved by dilute acid solutions when boiling. Solutions in acids are colourless, and show no absorption spectra. The emission spectrum of a solution in HClAq , obtained by help of the spark, shows several lines, the most conspicuous of which have the wave-lengths 6221, 5556, 5476, 5352, and 5334 (*v. Lecocq de Boisbaudran, C. R. 88, 1342*). S.G. 9.175. S.H. (0° – 100°) .0646 (Nilson, *l.c.*).

Hydrated ytterbium oxide. A white, gelatinous, but heavy pp. obtained by adding NH_3Aq to a solution of a salt of Yb; shrinks much when dried, and absorbs CO_2 from the air. Easily soluble in acids (Nilson, *l.c.*).

Ytterbium salts. Nilson (*l.c.*) prepared an oxalate, an acid selenite, and a sulphate; and Marignac (*C. R. 87, 578*) prepared a formate.

Ytterbium oxalate $\text{Yb}_2(\text{C}_2\text{O}_4)_3$. 1Aq. A white, microscopically crystalline powder; insoluble in water, scarcely soluble in dilute acids; unchanged in air; gives up part of its water at 100° . Prepared by adding oxalic acid to a warm solution of the sulphate.

Ytterbium selenite $\text{Yb}_2\text{O}_3 \cdot 4\text{SeO}_3 \cdot 5\text{aq}$. Obtained by adding $\text{Na}_2\text{SeO}_3\text{Aq}$ to a solution of $\text{Yb}_2(\text{SO}_4)_3$, washing the ppd. normal selenite, dissolving in water containing a large excess of H_2SeO_3 , evaporating nearly to dryness, and washing the residue with water. A white crystalline salt, insoluble in water. Loses $4\text{H}_2\text{O}$ at 100° .

Ytterbium sulphate $\text{Yb}_2(\text{SO}_4)_3$. Prepared by dissolving Yb_2O_3 in HNO_3Aq , adding $\text{H}_2\text{SO}_4\text{Aq}$, evaporating on a water-bath to drive off HNO_3 , then on a sand-bath, and finally over a flame at low redness till all H_2SO_4 is removed. An opaque, white solid. Dissolves in water when a large quantity is added at once; if a little is added much heat is produced, the salt combines with the water, and then dissolves very slowly when more water is added. Decomposed at a red heat, fully at a white heat. S.G. 3.793. S.H. .1039 at 0° to 100° .

A hydrated sulphate $\text{Yb}_2(\text{SO}_4)_3 \cdot 8\text{aq}$ was obtained by Nilson in large, white, lustrous prisms by evaporating a solution of $\text{Yb}_2(\text{SO}_4)_3$ in water at a gentle heat. M. M. P. M.

YTTRIUM. Y. At. w. c. 89.6. The name yttrium is given to the metal of an earth obtained from a few rare Swedish minerals. The separation of a new earth from a mineral found at Ytterby, in Sweden, was made by Gadolin in 1788. The existence of the new earth was confirmed in 1797 by Ekeberg, and the earth was called by him *yttria*. Subsequent researches carried on by Berzelius, Mosander, Scheerer, Berth, Delafontaine, Popp, Balf, a, Bunsen, Marignac, and others showed that the yttria of Gadolin and Ekeberg was a mixture of many oxides (*cf. EARTH, vol. ii. p. 456; SCANDIUM, vol.*

IV. p. 304; *YTTERIUM*, same vol. p. 879; and v. *infra*, *Homogeneity of Yttria*).

Occurrence.—About 30 to 85 p.c. of yttria, in combination with SiO_2 , is found in the exceedingly rare Swedish mineral *gadolinite*; some specimens of *orthite* also contain yttria, and the earth has also been found, in combination with Nb_2O_5 and Ta_2O_5 , in specimens of *euxenite*. The oxides that generally accompany yttria in these rare minerals are ceria, didymia, erbia, lanthana, lime, magnesia, soda, and oxide of iron.

Preparation of yttria.—The crude oxides of yttrium, erbium, &c., are separated from *gadolinite* by the method of Bahr a. Bunsen described under *Errium* (vol. ii. p. 457). Marigniac (*A. Ch.* [5] 14, 247) converted the oxides into nitrates, heated the nitrates in a Pt basin until red fumes came off freely; treated the residue with water, and separated the solution, which contained much Yt nitrate, from insoluble basic nitrates of Er, &c. He then evaporated the solution to dryness, heated again until partial decomposition was effected, again treated with water, poured off the solution, evaporated it to dryness, partially decomposed the solid nitrates by heat, and so on. After some hundred repetitions of these processes, approximately pure yttria was obtained. Auer von Welsbach (*M.* 4, 630) separated approximately pure yttria from the crude earths obtained from *gadolinite* by a long-continued series of operations based on the facts (1) that yttrium nitrate is less readily decomposed to basic salts than erbium nitrate when a fairly conc. solution of these nitrates is heated with the oxides of the metals made into a paste with water, and (2) that basic yttrium nitrates dissolve in a solution of the normal nitrates of Y and Er more readily than basic erbium nitrates.

References.—Gadolin (*Crell's Annal.* 1796 [1] 313); Ekeberg (*Scher. J.* 3, 187); Klaproth (*Scher. J.* 5, 531); Vauquelin (*Scher. J.* 5, 552); Berzelius (*Scher. J.* 16, 250, 404; and *Lehrbuch* [5th ed.], 2, 177); Berlin (*P.* 43, 105); Schoerer (*P.* 56, 493); Mosander (*P. M.* 23, 251); Popp (*A.* 131, 179); Delafontaine (*Ar. Sc.* [2] 21, 97; 22, 30; 25, 112; 51, 48; 61, 273); Bahr, (*A.* 135, 376); Bahr a. Bunsen (*A.* 137, 1); Cleve a. Höglund (*Bl.* [2] 18, 193, 279); Cleve (*Bl.* [2] 21, 844).

Preparation of yttrium.—The metal has not been obtained pure. Wöhler in 1828 (*P.* 13, 580) obtained impure yttrium by reducing the chloride by sodium. In 1864 Popp (*A.* 131, 179) dissolved yttria in HClAq , added NH_4ClAq , evaporated, separated and dried the double chloride of yttrium and ammonium thus formed, mixed this with Na, the double salt and the Na being arranged in alternate layers, heated the mixture in a closed crucible till action began and then allowed the reaction to proceed; washed the fused mass with water, separated unreacted yttria by levigation, washed the dark-grey powder that remained with water, and then with alcohol, and dried it over H_2SO_4 . In 1890 Winkler (*B.* 23, 787) obtained a black powder that decomposed water by heating yttria and finely divided Mg in the ratio $\text{Y}_2\text{O}_3:3\text{Mg}$ (*cf.* *Yttrium*, p. 882). Popp describes yttrium as a dark-grey powder resembling *ferrum redactum*, decomposing cold water slowly and hot water rapidly,

easily dissolved by dilute acids, including acetic acid, decomposing boiling KOHAc , and NH_4ClAq at the ordinary temperature, with evolution of H and NH_3 ; the metal burns brilliantly when heated on Pt foil; when heated in O it burns with a very dazzling light.

An examination of the emission spectrum of yttrium was made by Thalen: the most prominent lines observed had the wave-lengths 6191, 6431, 5987, 5971, 5662, 5496, 5102, 5205, 5200, 5088, 4900, 4881, 4854, 4374, and 4309 (*Konigl. Sw. Vetens. Acad. Handl.* 12).

The atomic weight of yttrium was determined by Berzelius, Delafontaine, Popp, Bunsen a. Bahr (*v. supra*, *References*) by analyses of the sulphate, or by transforming yttria into the sulphate; the values varied from 92.2 to 102.3. In 1873 Cleve a. Höglund (*v. B.* 6, 1467) made more accurate determinations by analysing purer specimens of $\text{Yt}(\text{SO}_4)_3$, and obtained the value 89.6.

Chemical relations of yttrium.—Assuming yttrium to be a homogeneous element with at. w. c. 89, it must be placed in Series 6 of Group III. in the periodic arrangement of the elements. This group contains the earth metals; yttrium is preceded in the even series family by Ba and Sr, and succeeded by La and Yb. A consideration of the position given to Y in the periodic classification shows that the element ought to closely resemble the other metals of the earths. Too little is known of the properties of many of the earth metals to allow of a detailed comparison of them one with another. A general account of the relations of these metals will be found in *Earth's METALS OF THE* (vol. ii. p. 424).

The homogeneity of yttria.—The properties described as belonging to yttria before 1885 were the properties of a mixture of at least five, and perhaps six, different bodies, according to Crookes (*C. N.* 51, 13, 155). Crookes subjected 'yttria' to a prolonged process of fractionation by ammonia (for a description of this method *v. Errium*, vol. ii. p. 423), and he then examined the phosphorescence spectra of various fractions. Crookes concludes that yttrium is a compound, or perhaps a very intimate mixture, of simpler bodies. For details of the phosphorescence spectra of the substances obtained by fractionating 'yttria' *v. METALS, RARE* (vol. iii. p. 248). By thirty-two fractionations of 'yttria' by ppm. with NH_4Aq , followed by twenty-six fractionations by ppm. with oxalic acid, Leebq de Boisbaudran (*C. R.* 103, 619 (1887)) obtained a white specimen of yttria which gave no phosphorescence spectrum when mixed with lime, and which, when converted into chloride, gave a spark spectrum, showing only the lines of yttrium.

Yttrium, bromide of, $\text{YBr}_3 \cdot 9\text{H}_2\text{O}$. Colourless, very deliquescent tablets; obtained by dissolving Y_2O_3 in HBrAq and concentrating (Cleve, *Bl.* [2] 18, 193). The anhydrous salt is obtained by Duboin (*C. R.* 107, 99, 248) by heating Y_2O_3 to redness on a support of gas-carbon in a current of CO and Br vapour. Very soluble in water or alcohol; insoluble in ether.

Yttrium, chloride of, $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$. Obtained by dissolving yttria in HClAq , evaporating to dryness on a water-bath; dissolving in alcohol, and evaporating over H_2SO_4 (Cleve, *l.c.*). Crystallises in large, colourless, very deliquescent,

rhombic prisms (C., Lc.). The anhydrous compound is formed by heating yttria to redness on a support of gas-carbon in a slow stream of CO and Cl (Duboin, Lc.). By evaporating a solution of yttria in HClAq with addition of NH_4Cl a double compound of YCl_3 and NH_4Cl is obtained; double compounds with KCl and NaCl are formed by fusing the constituent chlorides together. Popp (A. 181, 179) described the double compound $\text{YCl}_3 \cdot 3\text{HgCl}_2 \cdot 9\text{H}_2\text{O}$. Cleve (Bl. [2] 31, 195) described $\text{YCl}_3 \cdot \text{SnCl}_4 \cdot 8\text{H}_2\text{O}$.

Yttrium fluoride of $2\text{YF}_3 \cdot \text{H}_2\text{O}$. Obtained as a gelatinous pp. by adding HFAc , or solution of an alkali fluoride, to solution of a salt of yttrium (Cleve, Bl. [2] 18, 193).

Yttrium iodide of $(? \text{YI}_3)$. Deliquescent crystals, soluble in alcohol; obtained by evaporating a solution of yttria in HKAq (Berlin, P. 43, 105; no analyses given).

Yttrium oxides of. Besides yttria, Y_2O_3 , there probably exists another oxide, containing more oxygen.

YTTRIA Y_2O_3 . (Yttrium sesquioxide). A hydrate, probably $\text{Y}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$ (Popp, Lc.), is obtained, as a gelatinous pp. closely resembling hydrated alumina, by ppg. the solution of a salt of yttrium by ammonia. The oxide is formed by strongly heating this hydrate; also by decomposing by heat the carbonate, nitrate, or oxalate of yttrium in presence of air. Yttria is described as a heavy, white or almost white powder, S.G. 5.078 (Cleve, Lc.); 5.046 (Nilson a. Pettersson, B. 13, 1459). S.H. (0° - 100°) 1026 (N. a. P., Lc.). By heating amorphous yttria with CaCl_2 for some hours, and washing with warm water, Duboin (C. R. 107, 99, 243) obtained highly refractive crystals of Y_2O_3 , scarcely acted on by acids or by fused Na_2CO_3 . Yttria is a markedly basic oxide; it absorbs CO_2 from the air, and decomposes solutions of ammonium salts, giving off NH_3 . Yttria is insoluble in water; it dissolves slowly in cold HClAq, HNO_3 Aq, or H_2SO_4 Aq, but more rapidly on warming. By heating a mixture of yttria and finely-powdered Mg, in the ratio $\text{Y}_2\text{O}_3 : 3\text{Mg}$, Winkler (B. 23, 787) obtained a black powder which slowly gave off H from cold water, rapidly from hot water, and dissolved in dilute HClAq, with violent evolution of H.

YTTRIUM PEROXIDE. By adding H_2O_2 Aq and NH_4Aq to a solution of sulphate or nitrate of yttrium, Cleve (Bl. [2] 43, 53) obtained a white gelatinous pp. to which he gave the composition Y_2O_5 ; but this formula cannot be regarded as final.

Yttrium salts of. The salts which are formed by replacing the H of acids by yttrium belong to the form Y_2X_3 , where $\text{X} = 2\text{ClO}_4$, 2NO_3 , SO_4 , SO_3 , CO_3 , 3PO_4 , &c. Almost all the yttrium salts of oxyacids that have been prepared are normal salts; a basic nitrate, and an acid orthophosphate and selenate, are known. Many of the salts are obtained by dissolving yttria in acids and evaporating; those salts which are fusible, or but slightly soluble, in water are formed by ppn. from the nitrate or sulphate. The salts formed by ppn. are the arsenate, borate, carbonate, chromate, iodate and periodate, oxalate, phosphites, selenite and sulphite; besides these salts, the following salts of oxyacids are known, and are soluble in water: bromate, chlorate and perchlorate, nitrate, selenate, sulphate, thiosulphate and tungstate. A few double salts are known; the principal are $\text{Y}_2(\text{CO}_3)_3 \cdot \text{M}_2\text{CO}_3 \cdot x\text{H}_2\text{O}$, $\text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot 3\text{M}_2\text{C}_2\text{O}_4 \cdot x\text{H}_2\text{O}$, and $\text{Y}_2(\text{SO}_4)_3 \cdot m\text{M}_2\text{SO}_4 \cdot x\text{H}_2\text{O}$, where M = an alkali metal. Duboin (C. R. 107, 99, 243) obtained a silicate $\text{Y}_2\text{O}_3 \cdot \text{SiO}_2$ by very strongly heating a mixture of 3 pts. yttria with 90 pts. CaCl_2 , and washing with water. The yttrium salts of oxyacids have been examined, chiefly by Cleve (Bl. [2] 18, 193, 239; 21, 344; v. also Berlin, P. 43, 105; Högbon, Bl. [2] 42, 2; Popp, A. 131, 179).

Yttrium sulphide of. No compound of yttrium and sulphur has been isolated with certainty. Addition of $(\text{NH}_4)_2\text{SAc}$ or NH_4HSAc to a solution of a salt of yttrium ppts. hydrated oxide. By fusing yttria, S, and an alkali carbonate, and washing the fused mass with water, a yellowish-green solid is obtained that is insoluble in water, but is partly decomposed thereby to hydrated oxide and H_2S ; this solid dissolves in acids, giving off H_2S . The same solid seems to be obtained by strongly heating yttria in H laden with CS_2 . No compound of yttrium and S was obtained by heating yttria with Na_2S_2 . By heating YCl_3 in a stream of H_2S , HCl is given off, and a yellow powder remains, which is decomposed by water, with evolution of much H_2S (v. Popp, A. 131, 179). According to Popp (Lc.), the composition of this substance is Y_2S_3 .

By passing dry H_2S over a mixture of YCl_3 with excess of NaCl , heated to c. 1000° in a boat of gas-carbon, Duboin (C. R. 107, 99, 243) obtained a greenish, crystalline solid, which when washed with water left transparent, greenish lamellae of the double compound $\text{Y}_2\text{S}_3 \cdot \text{Na}_2\text{S}$. M. M. F. M.

ZANZALOIN & ALON.

ZEORIN $\text{C}_{12}\text{H}_{18}\text{O}$. [231?]. Occurs in the ethereal extract from *Zeora sordida* (Paterno, G. 7, 281, 508). Small pyramids with hexagonal base (from ether-alcohol), v. al. sol. alcohol and ether, insol. water. Neutral. Not attacked by alkalis or dilute acids.

ZINC. Zn. At. w. c. 65.8 (v. infra).

Mol. w. c. 65.8 at c. 1400° ; probably the same in solution in Hg (v. infra). Melts at 419° (determined by air thermometer; v. Meyer & Riddle, B. 26, 243); at 417.77° (determined by platinum thermometer, Callendar & Griffiths, C. N. 66, 1); for older determinations, giving

m.p. from 440° to 450° , v. Carnelley's *Melting- and Boiling-point Tables* (1, 14). Boils between 980° and 954° (Deville a. Troost, *C. R.* 90, 773); at 930° (Vielle, *C. R.* 94, 720; cf. Troost, *C. R.* 94, 788). S.G. c. 6.9 to 7.2 (v. Schaff, *A.* 107, 59; Kelscher, *B.* 14, 2750; Quinke, *P.* 135, 642; Spring, *B.* 16, 2724). V.D. 34.8 at c. 1400° (Mensching a. V. Meyer, *B.* 19, 3295). S.H. (0° to 100°) .0935 (Bunsen, *P.* 141, 1); (19° to 47°) .0932 (Kopp, *T.* 155, 71; cf. Schüller a. Wartha, *B.* 8, 1016). C.E.; if length of bar at $0^{\circ} = l^{\circ}$, then length at $t^{\circ} = (1 + \beta l)$; if volume at $0^{\circ} = V$, then volume at $t^{\circ} = (1 + \beta V)$; $\beta = .00002976$ from 0° to 100° (Matthiessen, *P. M.* [4] 32, 472). Heat of fusion for 1 kilo = 28,130 (Pérson, *A. Ch.* [3] 24, 129). T.C. (Ag = 100) 28.1 (Wiedemann, *P. M.* [4] 19, 243). E.C. (Hg at $0^{\circ} = 1$) 16.1 at 0° , 16.92 at 100° (Benoit, *P. M.* [4] 45, 314); 14.85 at 100° (Kirohoff a. Hanseman, *W.* 13, 406). Chief lines in emission spectrum 6360, 6100, 4924, 4911, 4809, 4722, 4679 (Huggins, *T.* 154, 139; cf. Thülen, *Détermin. des Longueurs d'Ondes des Raies Mécaniques* [Upsala, 1868]; and Ames, *P. M.* [5] 30, 33); for wave-lengths of lines of high refrangibility, v. Hartley a. Adeney (*T.* 1884 [1], 97). Zinc crystallises in tabular hexagonal plates, $a : c = 1.356425$ (Williams a. Burton, *Am.* 11, 219; cf. Schöla, *J. pr.* 89, 122; 96, 178; Sharples, *Am. S.* [3] 7, 223; Nöggerath, *P.* 39, 324; Nickles, *A. Ch.* [3] 22, 37; G. Rose, *B. D.* 1852, 26; *P.* 107, 448; Storer, *P. Am. A.* 6; Cooke, *Am. S.* 31, 191). The metal is probably dimorphous. H.C. [Zn, O] = 85.430 (Thomsen, *Th.* 8, 275). Refraction equivalent = 9.8 (Gladstone, *Ph.* 18, 49).

Historical.—That copper acquired a reddish colour, and that its properties were modified, by melting with certain ores, was known to the ancients and the alchemists; the ore with which copper was generally melted to form brass was called *cadmia fossilis*. The fact that a lustrous solid could be obtained by heating *cadmia fossilis* seems to have been known to the ancient writers on mineralogy. According to Kopp (*Geschichte der Chemie*, 4, 116), the earliest use of the word *zinc* is found in a writing of the fifteenth century attributed to Basil Valentine. Paracelsus, in the sixteenth century, speaks of zinc as a definite metal-like substance, and assigns it to the class of bastard or semi-metals. The name 'zinc' was applied during the seventeenth and eighteenth centuries alike to zinc ores and to the metal-like substances obtained from these ores. Boyle speaks of zinc, and also uses the word *spelter*, or *splauter*, a term of Indian origin according to Kopp. Tolerably pure zinc seems to have been obtained from zinc ores about 1720; probably by Henckel (v. Percy's *Metallurgy*, 1, 320).

Occurrence.—Zinc is found in small quantities; Becker (*J. M.* 1857, 698) and Phipon (*C. R.* 55, 218) noticed the occurrence of native zinc in Victoria. Considerable quantities of compounds of zinc occur in many places; the commonest ore are *calamine* (carbonate), *siliceous calamine* (silicate), *blende* (sulphide), and *red zinc ore* (oxide); aluminate, arsenate, phosphate, and sulphate of zinc are also found, but in smaller quantities. Small quantities of Cd compounds occur in most zinc ores. The

ash of a plant that grows on the waste heaps of the zinc works in Rhenish Prussia (*Viola calaminaria*) is said to contain compounds of zinc (Braun, *P.* 927 175). Zinc compounds have been found in some springs (v. Hillebrand, *U. S. Geology. Survey Bull.* No. 113 [1898]). Traces of zinc compounds have been found, according to Lechartier a. Bellamy (*C. R.* 84, 687), in the human liver, in calves' liver, in beef, hens' eggs, wheat, barley, maize, beans, and vetches.

Formation.—Zinc ore, generally carbonate or sulphide, is roasted in reverberatory calciners; the roasted ore is mixed with half its weight of powdered charcoal, coke, or anthracite, and heated in crucibles or retorts arranged so that the reduced metal distills from the impurities; the metal is condensed and collected in suitable vessels, and CO passes off. For details and descriptions of the different forms of apparatus, v. *DICTIONARY OF APPLIED CHEMISTRY*, vol. iii. p. 1042.

Preparation.—Commercial zinc generally contains from .5 to 3.3 p.c. lead, with c. .2 to .5 p.c. iron and cadmium, and small traces of arsenic.

Pure zinc was prepared by Reynolds a. Ramsay (*C. J.* 51, 854 [1887]) by dissolving zinc sold as free from common impurities in dilute H_2SO_4 , evaporating, crystallising the sulphate several times, electrolysis a solution of this salt, the metal being deposited on an electrode of Pt wire, dissolving the metal in dilute $HClAq$, ppg. $ZnO.H_2$ by NH_4Aq , dissolving the pp. in excess of NH_4Aq , and ppg. ZnS by H_2S ; the ZnS was dissolved in $HClAq$, and again ppd. from an ammoniacal solution by Li_2S ; the pp. was well washed, dissolved in pure dilute H_2SO_4 , and the sulphate obtained on crystallisation was re-crystallised several times; an aqueous solution of this sulphate was then electrolysed, using a Pt wire as electrode, and the metal was melted in a tube of hard glass from which the air had been exhausted. By distilling this metal *in vacuo* in a tube of hard glass, very pure zinc was obtained. Pullinger (*C. J.* 57, 816 [1890]) distilled zinc sold as 'chemically pure' in a hard glass tube, bent slightly towards the closed end, placed in a combustion furnace, the open end being connected with a good water-pump. By melting the distilled zinc in a tube of hard glass with a small bulb blown on the end, the part of the tube between the bulb and the wider portion containing the zinc being capillary, and the open end being connected with a water-pump, he obtained the zinc imperfectly bright, smooth, lustrous spheres free from hollows; the pump was stopped while the zinc was molten, and the increased pressure caused the molten metal to filter through the capillary tube into the bulb. For the preparation of pure zinc by electrolysis of an ammoniacal solution of the sulphate, v. Myers (*C. R.* 74, 195).

Soliba (*C. C.* 1834, 419) says that zinc can be obtained free from As and nearly free from iron by the combined interaction of S and water vapour. He mixes burnt gypsum with one-fourth its weight of S powder, moulds the moistened mixture into spheres about 5 cm. diameter, and sinks these to the bottom of a crucible containing molten zinc; vapours of

H₂S and S are given off, and the molten metal is thereby briskly agitated. When the reaction is completed, the little balls are taken out, the upper crust is removed, and the operation is repeated if necessary.

Zinc-dust is obtained either in the distillation of the metal, or, is not such fine division, by crushing and powdering the metal in an iron mortar at a temperature somewhat below the m.p. of zinc. The ZnO₂H₂ always present in specimens of zinc-dust may be removed by digesting with NH₄ClAq and then with NH₄Aq, and drying on a porous tile *in vacuo* (Carnegie, C. J. 53, 471).

Properties.—Zinc is a white metal, with a slight shade of blue; it is very lustrous when polished. Commercial zinc is brittle at the ordinary temperature, but it becomes malleable between 100° and 150°; at 210° it again becomes brittle, and at that temperature it can be finely powdered in a mortar. Pure zinc is said to be malleable at the ordinary temperature. Commercial zinc that has been heated to 100°–150° retains its malleability when it cools. Kahlischer (B. 14, 2747) noticed that rolled zinc ceased to give a ringing sound when struck after it was heated to c. 160°–300°, that it could then be bent easily, and that when bent it emitted a sound like the 'cry' of tin; he found that the zinc became crystalline, and the crystalline structure was more decided the higher the temperature; the S.G. was very slightly increased, and the electrical resistance was reduced by c. 3 p.c. Zinc is a softer metal than copper; its hardness is increased by rolling. The tensile strength of zinc varies much with the mode of preparation. Zinc crystallises easily, especially when pure; the form is that of hexagonal plates (for references *v. supra*, beginning of this article). Zinc melts at c. 420°, and boils somewhat below 1000° (*v. supra*). Molten zinc expands somewhat during solidification. The metal can be distilled at a full red heat; the vapour takes fire in the air, and burns with formation of ZnO and the production of a bright white light. Zinc exposed to the ordinary air becomes very gradually covered with a thin film of a basic carbonate which protects the mass of the metal from further corrosion; in pure dry air zinc is unchanged. Zinc dissolves in dilute acids, generally with evolution of H (*v. infra*, *Reactions with sulphuric and nitric acids*); it also dissolves in solutions of caustic potash or soda. When impure zinc is amalgamated it resists the action of acids. Zinc is not acted on by mineral lubricating oils; some of the commoner animal oils attack it slightly (*v. Redwood, C. S. I. 5, 362*). Zinc ppts. most of the other metals from their solutions; if a piece of impure zinc is dissolved in an acid, most of the metallic impurities (As, Cd, Cu, Pb, &c.) remain undissolved as long as undissolved zinc is present. Zinc combines directly with O, S, Se, Te, the halogens, and P; it forms alloys with many metals. Pure zinc does not decompose boiling water, but the commercial metal reacts and gives off H. Zinc-dust usually contains some ZnO₂H₂; it is said also to contain H, produced by the interaction of Zn and ZnO₂H₂ (*v. Greville Williams, C. N. 52, 205, 268*).

Atomic and molecular weights of zinc. In 1809 Gay-Lussac (*Mém. S. d'A.*, 2, 174) deter-

mined the weight of ZnO obtained by dissolving a determinate weight of zinc in nitric acid, evaporating to dryness, and strongly heating the residue; Berzelius in 1811 repeated the experiment of Gay-Lussac (G. A. 37, 400; *v. also P.*, 8, 184); and in 1843 Erdmann made similar experiments (*v. Berzelius' Lehrbuch*, 3, 1219). The values obtained for the at. w. of zinc were 65.39 (G.-L.), 65.41 (B.), and 64.94 and 64.88 (E.). In 1844 Favre decomposed ZnCO₃ by heating in air, and determined the weights of ZnO and CO₂ produced; the value 65.85 was thus obtained for the at. w. of zinc. In the same year Favre obtained the value 66.78 by dissolving zinc in dilute H₂SO₄Aq, burning the H given off by passing it over hot CuO, and weighing the water thus produced (A. Ch. [3] 10, 163). In 1884 Marignac determined the Cl and the Zn in ZnCl₂·2KCl, and obtained the value 65.18 for the at. w. of zinc (A. Ch. [6] 1, 309; *v. also* Baubigny, C. R. 97, 908 [1883]). By dissolving zinc in dilute H₂SO₄Aq and measuring the H given off, van der Plaats concluded that the at. w. of zinc is 65.18 (C. R. 100, 52 [1885]). Reynolds a. Ramsay, in 1887, by measuring the H given off by the interaction between very pure zinc and H₂SO₄Aq, obtained the value 65.48 (C. J. 51, 854). By oxidising zinc to ZnO, by HNO₃Aq, in 1888, Moxse a. Burton, obtained the value 65.1 (Am. 10, 311). In 1889 Gladstone a. Hibbert (C. J. 55, 443) determined the ratio of zinc dissolved to silver deposited by one and the same electric current; taking the at. w. of silver as 107.66 (the value adopted in this Dictionary) the at. w. of zinc was found to be 65.29.

In 1886 Mensching a. V. Meyer (B. 19, 8295) found the V.D. of zinc at c. 1400° to be 34.3, a number which shows that the gaseous molecule of zinc is monatomic. Ramsay, in 1889, determined the lowering of the vapour pressure of Hg produced by dissolving zinc therein (C. J. 55, 521); assuming that equal volumes of dilute solutions contain equal numbers of molecules, and that the molecular weight of liquid Hg is 200, Ramsay's results indicate that the molecules of zinc in dilute solutions of this metal in Hg are monatomic. The experiments of Heycock a. Neville (C. J. 57, 376 [1890], and 61, 888 [1892]) on the lowering of the freezing-points of Bi, Cd, Pb, Sn, and Na by solution of zinc in these metals tend to confirm the conclusion that the molecule of zinc in dilute solutions in these metals is monatomic.

Chemical relations of zinc. Zinc is the second odd-series member of Group II. in the periodic classification of the elements. Zinc is preceded in the odd series of this group by Mg and is followed by Cd, —, and Hg; the members of the even series of Group II. are Be, Ca, Sr, Ba, —. Zinc is the second member of series 5; it is preceded in this series by Cu, and is succeeded by Ga, Ge, As, Se, and Br. The general chemical character of zinc is that of a metal; its oxide ZnO is basic, its chloride ZnCl₂ is volatilisable without decomposition. No acids are known containing zinc, and the molecule of the element is monatomic. The fact that compounds of ZnO and K₂O are obtained by dissolving ZnO₂H₂ in KOHAq and adding alcohol shows that the hydroxide of the metal has feebly marked acidic properties, and the iso-

tion of a number of oxychlorides and basic carbonates, nitrates, and sulphates illustrates the fact that zinc is less positive than Mg, which is the first member of the zinc family of Group II. For a general account of the properties of the family of which zinc forms a member v. MANGANESE GROUP OF ELEMENTS, vol. iii. p. 163. The atom of zinc is divalent in the gaseous molecules of its compounds.

Reactions and Combinations.—1. Zinc is unchanged in pure dry air; in ordinary air the surface layers are slowly converted into a basic carbonate, which protects the metal beneath. Heated strongly in air or oxygen, zinc burns to ZnO .—2. Heating zinc in bromine, chlorine, or iodine produces ZnBr_2 , ZnCl_2 , or ZnI_2 .—3. When zinc is heated in phosphorus vapour, phosphide of zinc (q. v., p. 890) is formed.—4. By heating zinc with selenium vapour, a compound of Zn and Se is formed (v. ZINC SELENIDE, p. 890).—5. Zinc combines with tellurium when the elements are heated together (v. ZINC TELLURIDE, p. 891).—6. Sulphur and zinc combine when a mixture of these elements is very strongly compressed (Spring, B. 16, 1000).—7. Zinc decomposes water at a red heat. Commercial samples of zinc decompose water at 100° (L'Hôte, C. R. 101, 1153).—8. ZnS is formed by strongly heating zinc in a stream of hydrogen sulphide; when hydrogen selenide is used the product is ZnSe , and by heating the metal in hydrogen telluride ZnTe is formed (v. Margottet, C. R. 84, 1293).—9. Zinc is said to reduce carbon monoxide at a very high temperature.—10. Zinc is superficially oxidised by heating to dull redness in nitric oxide (Sibbier a. Senderens, C. R. 114, 1423). Oxidation in nitrogen dioxide (NO_2) is effected at 300° (S. a. S., C. R. 115, 236).—11. Many metallic oxides are reduced by heating with zinc.—12. Zinc reacts with sulphurous acid solution; according to Schweizer (v. C. N. 23, 293), the products are ZnSO_4 , along with $\text{H}_2\text{S}_2\text{O}_4\text{Aq}$, $\text{H}_2\text{S}_2\text{O}_6\text{Aq}$, and S.—13. Zinc dissolves in hydrochloric acid, giving off H and forming ZnCl_2 . Reynolds a. Ramsay (C. J. 51, 857) say that pure zinc scarcely reacts with boiling hydrochloric acid. For reactions of zinc with sulphuric and nitric acids, v. *infra*.—14. Zinc dissolves slowly in hot solutions of caustic soda or potash, giving off H, and forming $\text{ZnO} \cdot x\text{M}_2\text{O}$ (cf. ZINC HYDROXIDE, p. 888); the reaction is much hastened by adding iron or Pt along with the zinc.—15. Many metallic salts in solution are reduced by zinc, with ppn. of the metals, e.g. salts of As, Cd, Cu, and Pb.—16. When Zinc dust is shaken with an aqueous solution of ferric chloride, the whole of the ferric salt is very rapidly reduced to ferrous chloride (for details of the application of this reaction in the estimation of ferric iron, v. Carnegie, C. J. 53, 468 [1888]).—17. According to Siersch (J. 1887, 257), zinc dissolves in sodium chloride solution, forming $\text{ZnCl}_2 \cdot 2\text{NaClAq}$, ZnO , and H.—18. Pommardé (J. pr. 73, 496) says that nearly all chlorides and fluorides are reduced by reacting with vapour of zinc in an atmosphere of H.—19. By heating to redness a mixture of zinc filings and sodium metaphosphates, Hoeslet (A. 100, 99) probably obtained phosphides of zinc (v. ZINC PHOSPHIDES, p. 890).—20. Zinc reacts with sodium hydrogen sulphite solution,

forming ZnSO_4 , $\text{Na}_2\text{S}_2\text{O}_4\text{Aq}$, and $\text{Na}_2\text{SO}_4\text{Aq}$ (v. HYPOSULPHITES, this vol. p. 593).—21. By heating zinc with zinc sulphide in an exhausted tube, some of the ZnS is carried forward and deposited in the front part of the tube; probably at a high temperature ZnS is decomposed, and there exist offy Zn and S, and at a lower temperature these recombine to form ZnS (Morse a. White, Am. 11, 348). A similar phenomenon is noticed on heating zinc with zinc oxide (M. a. W., l.c. p. 258).—22. ZnS is formed by strongly heating zinc and mercuric sulphide or zinc and potassium polysulphides (v. ZINC SULPHIDE, p. 890).

When strips of zinc-foil are immersed in CuSO_4Aq , a deposit of finely-divided Cu is formed on the zinc. This copper-zinc couple is an energetic reducing agent; KClO_4Aq is reduced to KClAq , KNO_3Aq to KNO_2Aq and NH_4Aq , $\text{K}_2\text{FeCy}_6\text{Aq}$ to $\text{K}_2\text{FeCy}_5\text{Aq}$, SO_2Aq to S, $\text{As}_2\text{O}_3\text{Aq}$ to AsH_3 , $\text{C}_2\text{H}_5\text{NO}_2$ (in alcohol) to $\text{C}_2\text{H}_5\text{NH}_2$, &c. (v. Gladstone a. Tribe, C. J. 33, 306).

Reactions of zinc with sulphuric and nitric acids. Commercial zinc dissolves easily in dilute $\text{H}_2\text{SO}_4\text{Aq}$, with formation of ZnSO_4Aq and evolution of H. In 1830 De la Rive noticed that very little action took place between approximately pure zinc and $\text{H}_2\text{SO}_4\text{Aq}$; this fact has been confirmed by other experimenters. Reynolds a. Ramsay (C. J. 51, 857 [1887]) found that zinc prepared by repeated electrolysis of the sulphate and distillation *in vacuo* scarcely reacted with $\text{H}_2\text{SO}_4\text{Aq}$; L'Hôte (C. R. 101, 1153) also asserted that pure zinc does not react with $\text{H}_2\text{SO}_4\text{Aq}$. Divers a. Shimidzu (C. J. 47, 698 [1885]) observed very great differences between the rate of action of the same $\text{H}_2\text{SO}_4\text{Aq}$ on sheets of commercial zinc of the same size. Pullinger in 1890 (C. J. 57, 815), and Weeren in 1891 (B. 24, 1785), made somewhat elaborate investigations into the connections between the conditions and the rate of the interaction of zinc and $\text{H}_2\text{SO}_4\text{Aq}$.

Pullinger used 'pure' sulphuric acid diluted with three times its weight of water; and zinc prepared by distilling that sold as 'chemically pure' *in vacuo* and casting in balls under pressure to prevent the formation of cracks or hollows (v. *supra*, Preparation of zinc, p. 885). He found that when the surface of the zinc was very smooth this was best accomplished by immersing in aqua regia for 10 or 15 seconds, and washing with water—and the acid was boiled for some hours before the experiment, there was practically no reaction at 20° – 25° (spheres of zinc weighing c. 2½ g. lost from 5 to 6 mgns. in 20 hours). Pullinger found that the presence of small quantities of H_2S , SO_2 , or $\text{H}_2\text{S}_2\text{O}_4\text{Aq}$ did not affect the weight of zinc dissolved by the boiled $\text{H}_2\text{SO}_4\text{Aq}$; addition of some H_2O_2 materially increased the rate of action; and $\text{H}_2\text{SO}_4\text{Aq}$ that had been electrolysed before use dissolved from four to ten times more zinc than some of the same acid that had not been electrolysed; addition of a few drops of HNO_3Aq considerably increased the action; when a few drops of HClAq were added to the $\text{H}_2\text{SO}_4\text{Aq}$ practically no action occurred. P. supposed that all the 'pure' acid used by him contained traces of an oxidising substance, probably $\text{H}_2\text{S}_2\text{O}_8$, and that the solvent action was due to this. P.

insists on the important connection between the rate of action and the smoothness or roughness of the surface of the zinc used. But he concludes that 'in all probability pure dilute sulphuric acid would, at ordinary temperatures, be entirely without action upon metallic zinc, whether the surface of the latter were rough or smooth.'

Weeren used zinc which he found to be chemically pure by analysis; he gives no account of his method of preparation nor any details of his analytical results. W. found that the weight of pure zinc dissolved by pure $\text{H}_2\text{SO}_4\text{Aq}$ (1:20) at the ordinary temperature, and under a pressure of 10 mm., was a. ten times greater than the weight dissolved at 760 mm. pressure; but the weights of impure zinc dissolved at the two pressures were almost the same. The pure zinc used by W. dissolved fairly rapidly in boiling $\text{H}_2\text{SO}_4\text{Aq}$; in one case when 2.1 mgm. dissolved at 0° after thirty minutes' action, 122 mgm. dissolved in the boiling acid. W. found that the solubility of his pure zinc increased very slowly as temperature rose up to within 1° of the b.p. of the acid used, but that when ebullition actually began the solubility of the zinc suddenly increased; the weight of pure zinc dissolved by $\text{H}_2\text{SO}_4\text{Aq}$ at 100° and boiling, was a. sixteen times greater than the weight of the same zinc dissolved by the same acid at 100° but kept from actually boiling by pressure. On the other hand, W. noticed that as much impure zinc dissolved at 100° when the acid was boiling as when it was prevented by pressure from boiling. Addition of oxidisers, CrO_3 or H_2O_2 , enormously increased (c. 300 times) the solubility of pure zinc in $\text{H}_2\text{SO}_4\text{Aq}$ at $18^\circ\text{--}20^\circ$, but only slightly increased (c. six times) the solubility of impure zinc. W. supposes that when pure zinc is immersed in pure $\text{H}_2\text{SO}_4\text{Aq}$ a slight reaction occurs, and that the H produced is attracted to and held firmly on the surface of the zinc, and that the reaction ceases because the surface of the metal is protected by the layer of H. Increase of temperature does not appreciably affect the rate of action, because the layer of H remains fixed to the surface of the zinc, but when the acid boils the H is removed and rapid dissolution occurs; any conditions which remove the layer of H increase the solubility of the zinc. W. supposes that the rate of dissolution of impure zinc in $\text{H}_2\text{SO}_4\text{Aq}$ is not much affected by boiling, presence of oxidisers, &c., because H is not given off at the surface of the zinc, but at the surface of the more negative impurities. The rapid solution of zinc in HNO_3Aq is connected, according to W., with the rapid oxidation of the H produced at the surface of the zinc, and hence the production of a layer of water on the surface of the metal which destroys the attraction between the zinc and any H that may escape oxidation.

As regards the products of the interaction of zinc and sulphuric acid, when the acid is fairly concentrated (c. $\text{H}_2\text{SO}_4\text{H}_2\text{O}$ to c. H_2SO_4) SO_2 is given off, and at moderately high temperatures H_2S and S are also produced (v. Calvert a. Johnson, *C. J.* [2] 4, 435 [1867]). A qualitative examination of the products by Pattison Muir a. Adie (*C. J.* 58, 47 [1889]) showed that ZnSO_4 is the only salt of zinc produced, with any concen-

tration of acid, and at any temperature up to the b.p. of the acid used; that with approximately pure zinc little or no SO_2 or H_2S is formed unless the temperature be high; and that the purer the zinc the less is the quantity of S produced (*cf.* Ditte, *A. Ch.* [6] 19, 58).

The products of the interaction of zinc and nitric acid are $\text{Zn(NO}_3)_2\text{Aq}$, $\text{Zn(NO}_3)_2\text{Aq}$, $\text{NH}_4\text{NO}_3\text{Aq}$ and $\text{NH}_4\text{NO}_3\text{Aq}$, and NO , N_2O , and N_2 . Acworth found that when HNO_3Aq reacts with zinc in presence of $(\text{NH}_4)_2\text{NO}_3$, the chief gaseous product is N (along with some N_2O and NO) (*C. J.* 28, 828 [1875]). Acworth a. Armstrong studied the reaction of HNO_3Aq and Zn more fully in 1878 (*C. J.* 32, 54), and found that the only gaseous products were N , N_2O , and NO (*cf.* Deville, *C. R.* 70, 22, 550 [1870]). According to Divers (*C. J.* 43, 443 [1883]), a little NH_4OH is formed when cold HNO_3Aq (3 to 4 p.c.) is poured on to granulated zinc and quickly poured off again. Divers a. Shimidzu (*C. J.* 47, 597 [1885]) found that considerable quantities of NH_4OH are produced by the combined reaction of HNO_3Aq and $\text{H}_2\text{SO}_4\text{Aq}$, or HNO_3Aq and HClAq , on zinc (v. Hydroxylamine, *Formation*, vol. ii. p. 734). Divers (l.c.) thought that zinc does not form $\text{Zn(NO}_3)_2$ by a direct reaction with HNO_3Aq , but by interacting with some of the $\text{Zn(NO}_3)_2$ formed by the primary action of the metal on the acid. The products of the interaction of zinc and HNO_3Aq have been examined recently by Montemartini (*G.* 22 [1], 277 [1892]), who says that free H is not produced (he also says that no NH_4OH is formed), and that in addition to nitrate and nitrite of zinc and ammonium, hyponitrite is also produced; the gaseous products, according to M., are N_2O , NO , NO_2 , and N ; there is no nitrous acid formed, says M., if the HNO_3Aq contains more than 30 p.c. HNO_3 , and no NO_2 if less than 30 p.c. HNO_3 is present. M. also gives determinations of the quantities of the various products at different temperatures, and of the rate of reaction with different concentrations of HNO_3Aq (*Abstract in C. J.* 62, 1279 [1892]).

Zinc alloys of. Alloys of zinc have been formed with most metals by fusing the constituents together; the alloys are generally hard, some of them are brittle. With antimony, two crystalline alloys are formed by melting the metals together, in the ratios 3Zn:2Sb and Zn:Sb , and allowing to cool very slowly; Cooke (*Ann. S.* [2] 18, 229; 20, 222) formulates these alloys as Zn_3Sb and ZnSb , respectively. These alloys react with water and give off H. Alloys with arsenic are formed by heating together Zn and As, or Zn and As_2O_3 , or by heating Zn in vapour of As_2 and H; by the last method Descamps (*C. R.* 86, 1022, 1065) obtained crystals agreeing in composition with the formula Zn_3As_2 . Spring (*B.* 16, 324) formed an alloy by compressing Zn and As, in the ratio 3Zn:2As , at 6,500 atmospheres. Zinc alloys with bismuth when the metals are melted together, but on cooling two layers are formed, the upper containing zinc with c. 2 p.c. Bi, and the lower Bi with from 5 to 14 p.c. zinc. An alloy of zinc with bismuth and lead (3 pts. Zn, 5 pts. Bi, and 5 pts. Pb) melts at 94.5° . For descriptions of alloys with calcium v. Caron (*C. R.* 48, 440, 50, 547); Wöhler (*J.* 133, 253); and Norton a. Twissell

(*Ann. J.* 10, 70). Brass is composed of alloys of zinc with copper (v. vol. ii. p. 254; and for details v. DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 1052). Alloys of zinc with copper and nickel form German silver; most modern bronzes are alloys of zinc with copper and tin (v. vol. ii. p. 254; and for details v. DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 838). Zinc alloys with iron (for details v. DICTIONARY OF APPLIED CHEMISTRY, vol. iii. p. 1051). For alloys with lead v. vol. iii. p. 125 (also Krant, *S. U. I.* 5, 537). Alloys with lead and tin are mentioned in vol. iii. p. 125 (v. also Wright a. Thompson, *Pr.* 48, 25). For alloys with magnesium v. Parkinson (*J. pr.* 101, 375). Zinc and mercury form a number of amalgams, which are brittle when a little Hg is present and paste when much Hg is present (for references v. *S. C. I.* 9, 512). For alloys with platinum v. this vol. p. 288. For alloys with silver v. Wright a. Thompson (*Pr.* 48, 25).

For an account of the formation of zinc alloys by immersing zinc in various metallic solutions v. Mylius a. Fromm (*B.* 27, 630 [1894]).

Zinc, amide of, $Zn(NH_2)_2$. This compound was obtained by Frankland (*Pr.* 8, 502) by passing dry NH_3 into an ethereal solution of $ZnEt_2$. A white, amorphous powder; unchanged at 200° , but decomposed at a red heat to Zn_3N_2 (v. ZINC NITRIDE, p. 889) and NH_3 ; reacts with water to form ZnO, H_2 , and NH_3 .

Zinc, bromide of, $ZnBr_2$. Formula probably molecule, from analogy of $ZnCl_2$. S.G. 3.643 at 10° (Bödeker). Melts at 394° (Carnelley, *C. J.* 33, 277). Boils at 695° to 699° (C. a. Williams, *C. J.* 33, 283); at 650° (Freyer a. V. Meyer, *B.* 25, 622). H.F. [Zn, Br] = 75,930 (*Th.* 3, 275).

Preparation.—1. Zinc filings are heated to dull redness in a stream of H_2 vapour.—2. Zinc, or ZnO, H_2 , is dissolved in a slight excess of $HBrAq$, the solution is evaporated to dryness, and the dry residue is sublimed out of contact with air.

Properties and Reactions.—White needles; very deliquescent. Easily soluble in water, alcohol, or ether (v. Berthelot, *J. Ph.* 14, 610). Thomsen gives [$ZnBr_2, Aq$] = 15,030 (*Th.* 3, 275). Aqueous solutions of $ZnBr_2$ of different concentrations have the following specific gravities according to Kremers (*P.* 108, 115):—

S.G. $ZnBr_2, Aq$ at 19.5° .	P.c. $ZnBr_2$.
1.1849	18.3
1.3519	34.7
1.5276	43.2
1.7082	52.6
1.8525	59.1
2.1027	68.0

Combinations.—1. With ammonia to form a series of compounds. These compounds were examined by Rammelsberg (*P.* 55, 240), and, more recently, by André (*Bl.* [2] 59, 398 [1883]). By dissolving $ZnBr_2$ in NH_3, Aq under different conditions, A. obtained (1) $ZnBr_2 \cdot 2NH_3 \cdot H_2O$, (2) $3ZnBr_2 \cdot 8NH_3 \cdot 2H_2O$, (3) $3ZnBr_2 \cdot 10NH_3 \cdot H_2O$, and (4) $ZnBr_2 \cdot 5NH_3$; by saturating hot $NH_3, BrAq$ with ZnO , he obtained $3ZnBr_2 \cdot 6NH_3 \cdot 2H_2O$.—2. With caesium bromide, to form $ZnBr_2 \cdot 8CsBr$ and $ZnBr_2 \cdot 2CsBr$ (Wells a. Campbell, *Zeit. f. anorg. Chemie*, 5, 278).

Zinc, chloride of, $ZnCl_2$. Mol. w. c. 136. Melts at 262° (Braun, *P.* 154, 190). Boils at 708° to 719° (Carnelley a. Williams, *C. J.* 33, 284); at 730° (Freyer a. V. Meyer, *B.* 25, 622). S.G. 2.753 at 13° (Bödeker). V.D. at 890° to 907° = 66 (F. a. M., &c.). H.F. [Zn, Cl] = 97,210 (*Th.* 3, 275).

Formation.—1. By heating zinc filings in Cl_2 .—2. By heating a mixture of 2 pts. $HgCl_2$ and 1 pt. zinc filings in a retort.—3. By distilling a mixture of equal pts. $ZnSO_4$ and $CaOH_2$, or a mixture of 1 pt. ZnO and 2 pts. NH_4Cl .—4. By dissolving zinc, or ZnO, H_2 , in $HClAq$, evaporating to dryness, and heating the residue in a retort.

Preparation.—1. Zinc filings are heated in a small retort in a stream of Cl_2 ; the product is distilled.—2. $ZnCl_2$, or ZnO, H_2 , is dissolved in a slight excess of $HClAq$; the solution is evaporated to dryness, and the residue is distilled from a small retort.

Properties and Reactions.—A white, semi-transparent, crystalline, very caustic solid; very deliquescent. Easily soluble in water, also in alcohol. Thomsen gives [$ZnCl_2, Aq$] = 15,630 (*Th.* 3, 275). Sublimes at a red heat. An aqueous solution is partly decomposed on evaporation, giving oxychlorides (v.v.). Oxychlorides are also formed by heating a solution of $ZnCl_2$ in $HClAq$ with ZnO , also with HgO or PbO . Kremers (*P.* 105, 360) gives the following data:

S.G. $ZnCl_2, Aq$	P.c. $ZnCl_2$
1.1275	13.8
1.2466	25.8
1.3869	37.5
1.5551	49.2

A conc. solution of $ZnCl_2$ is often used as a bath for maintaining fairly high constant temperatures. Dry $ZnCl_2$ is used as a caustic; also as a dehydrating agent; a dilute aqueous solution is employed as an antiseptic.

Combinations.—1. With water. By keeping $ZnCl_2, Aq$ containing 70.5 p.c. $ZnCl_2$ at 0° for 24 hours, Engel (*C. R.* 102, 111) obtained large crystals of the trihydrate, $ZnCl_2 \cdot 3H_2O$, melting at 7° . When $ZnCl_2, Aq$ containing 79.9 p.c. $ZnCl_2$ at 0° is kept for a long time it solidifies; on heating to 16° a part melts and a part remains solid; the liquid part is the dihydrate $ZnCl_2 \cdot 2H_2O$, and the solid part is the hydrate $2ZnCl_2 \cdot 3H_2O$ (E., l.c.). By heating a syrupy solution of $ZnCl_2$ with a little $HClAq$, Schindler (*Mag. Pharm.* 36, 45) obtained octahedral crystals of the monohydrate $ZnCl_2 \cdot H_2O$. According to Engel (l.c.), the hydrate obtained by S. was $2ZnCl_2 \cdot 3H_2O$.—2. With hydrogen chloride and water. Engel (*M.* 5, 432) obtained the compounds $2ZnCl_2 \cdot HCl \cdot 2H_2O$ and $ZnCl_2 \cdot HCl \cdot 2H_2O$ by passing HCl gas into $ZnCl_2, Aq$, and adding zinc from time to time, and, when the solution had the S.G. of 2.0, cooling to 0° .—3. Various compounds of $ZnCl_2$ with ammonia have been described; the formulae $ZnCl_2 \cdot NH_3$, $ZnCl_2 \cdot 2NH_3$, $2(ZnCl_2 \cdot 2NH_3) \cdot H_2O$, $ZnCl_2 \cdot 4NH_3 \cdot H_2O$, and $ZnCl_2 \cdot 6NH_3 \cdot H_2O$ have been given to compounds obtained by dissolving $ZnCl_2$ in NH_3, Aq , passing in NH_3 , and evaporating under different conditions (v. Marignac, *Ann. M.* [5] 12, 1; Divers, *C. N.* 18, 13; Puzoznik, *P.* 142, 467; Davis, *C. N.* 25, 265; André, *A. Ch.* [6] 3, 84, 98; Thoms, *B.* 20,

748).—4. Lang (*B.* 21, 1578) described a compound with pyridine, $\text{ZnCl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$.—5. ZnCl_2 combines with *alkali chlorides*. Compounds, $\text{ZnCl}_2 \cdot \text{NH}_4\text{Cl} \cdot \text{H}_2\text{O}$, $\text{ZnCl}_2 \cdot 2\text{NH}_4\text{Cl} \cdot 2\text{H}_2\text{O}$, and $\text{ZnCl}_2 \cdot 3\text{NH}_4\text{Cl}$ are described by Schindler (*Mag. Pharm.* 36, 46), Marignac (*J.* 1857, 217), Rammeisberg (*P.* 94, 508), and Hantz (*A.* 68, 287). A compound $\text{ZnCl}_2 \cdot 2\text{KCl}$ is described by R. (*l.c.*) and M. (*l.c.*); and a compound $\text{ZnCl}_2 \cdot 2\text{NaCl} \cdot 3\text{H}_2\text{O}$ by M. (*l.c.*). Wells & Campbell (*Zeit. f. anorg. Chem.* 5, 273) describe two compounds with CaCl_2 , to which they give the formulae $\text{ZnCl}_2 \cdot 2\text{CaCl}_2$ and $\text{ZnCl}_2 \cdot 3\text{CaCl}_2$.—6. With *zinc oxide*, v. *Oxychlorides*, p. 891.

A solution of zinc in conc. HCl aq. to which as much NH_4Cl has been added as the weight of zinc dissolved, is used for cleaning the surfaces of metals that are to be soldered together; any oxide on the metallic surfaces reacts with the NH_4Cl present to form chloride which dissolves in the ZnCl_2 solution.

Zinc, cyanide of, and double zinc cyanides; v. vol. ii. p. 347. For details regarding the conditions of formation and the properties of *zinc-mercuric cyanide*, v. Dunstan, *C. J.* 61, 666 [1892].

Zinc, ferrocyanide of; v. vol. ii. p. 337.

Zinc, fluoride of, ZnF_2 . Formula probably molecular, from analogy of ZnCl_2 . Formed by heating zinc or ZnO to redness in a stream of dry HF ; also by the interaction of fused ZnCl_2 and dry HF at 800° to 900° ; also by heating the hydrated salt to redness in dry HF (Poulenc, *C. R.* 116, 581 [1893]). The *tetrahydrate* $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ is obtained by evaporating a solution of zinc in HFAg , and crystallising. The salt ZnF_2 crystallises i.e., colourless needles, probably monoclinic. S.G. 4.84 at 15° ; the crystals act strongly on polarised light (P., *l.c.*). Clarke (*Ann. S.* [3] 13, 291) gives S.G. of ZnF_2 as 4.556 at 17° , and 4.612 at 12° ; and the S.G. of $\text{ZnF}_2 \cdot 4\text{H}_2\text{O}$ as 2.567 at 10° and 2.535 at 12° . ZnF_2 is slightly soluble in cold, more soluble in hot water; it is insoluble in alcohol at 95° ; soluble in boiling HClAq , $\text{H}_2\text{SO}_4\text{aq}$, or HNO_3aq (P., *l.c.*). Heated in air, or to redness in steam, it is wholly changed to ZnO ; fusion with alkali carbonates produces ZnO and alkali fluorides; heating with H_2S forms ZnS , and with HCl forms ZnCl_2 . It is reduced by H at a red heat (P., *l.c.*). ZnF_2 forms *double salts* with AlF_3 and with alkali fluorides. Berzelius (*P.* 1, 26) described the salts $\text{ZnF}_2 \cdot 2\text{AlF}_3$ and $\text{ZnF}_2 \cdot 2\text{KF}$; and Wagner (*B.* 19, 896) the salts $\text{ZnF}_2 \cdot 2\text{NH}_4\text{F}$, 2aq , $\text{ZnF}_2 \cdot \text{KF}$, and $\text{ZnF}_2 \cdot \text{NaF}$. The compound $\text{ZnF}_2 \cdot \text{ZrF}_2 \cdot 6\text{aq}$ (= $\text{ZnZrF}_6 \cdot 6\text{aq}$) is described by Marignac (*A. Ch.* [3] 60, 257); S.G. 2.255 at 12° (Topsøe, *C. O.* 4, 76). For $\text{ZnF}_2 \cdot \text{SiF}_6$, v. *Zinc silicofluoride*, p. 890.

Zinc, hypophosphide of, ZnPH_2 . A white, friable solid having this composition was obtained by Dröschel & Finkelstein (*B.* 4, 352) by passing dry PH_3 into a cooled ethereal solution of ZnEt_2 . The compound can be kept in a closed vessel; in air it absorbs moisture and rapidly decomposes, giving off PH_3 .

Zinc, hydrosulphide of. According to Thomsen (*B.* 11, 2044 [1878]), the pp. obtained by mixing NaHSaAq and ZnSO_4aq , in equivalent quantities, is probably a hydrosulphide of zinc (no analysis or formula given). Addition of

two equivalents of NaSH in solution to an equivalent of ZnSO_4 in solution produces no pp., but the solution gives a pp. of ZnS or hydrosulphide on standing, or on addition of acid or soda (T., *l.c.*). According to von Zotta (*M.* 10, 807 [1890]), the pp. supposed by Thomsen to be zinc hydrosulphide has the composition $\text{ZnS} \cdot \text{H}_2 \cdot 2\text{ZnS}$. When four equivalents of NaSH are added to one equivalent of ZnSO_4 , both in solution, and the clear solution is boiled, or treated with acid or alkali, a pp. of $\text{ZnS} \cdot \text{H}_2 \cdot 2\text{ZnS}$ is obtained (von Z., *l.c.*). Linder & Picton (*C. J.* 61, 130 [1892]) obtained evidence in favour of the existence of compounds of Zn , S , and H , probably $7\text{ZnS} \cdot \text{H}_2 \cdot \text{S}$ and $12\text{ZnS} \cdot \text{H}_2 \cdot \text{S}$, by passing H_2S into water at 0° with $\text{ZnO} \cdot \text{H}_2$ in suspension; they failed to isolate a definite compound with certainty.

Zinc, hydroxide of, $\text{ZnO} \cdot \text{H}_2$. (*Zinc hydrate*, *hydrated zinc oxide*.) Obtained, as a white flocculent pp., by adding to solution of a salt of zinc rather less KOHaq than is sufficient to decompose the whole of the salt, washing thoroughly, and drying at a low temperature. According to Ville (*C. R.* 101, 375), $\text{ZnO} \cdot \text{H}_2$ is obtained in crystals by shaking very finely-powdered ZnCO_3 , or basic carbonate, with twice as much KOH in 10 p.c. solution as is theoretically required for the decomposition of the carbonate; formation of crystals of $\text{ZnO} \cdot \text{H}_2$ begins at once, and is complete after twenty to thirty minutes. $\text{ZnO} \cdot \text{H}_2$ is said to be obtained in lustrous rhombic prisms by immersing zinc in contact with iron or copper in NH_4Aq (Nickles, *A. Ch.* [3] 22, 31; Carnu, *Bl.* 5, 64 [1863]). Bödeker (*A.* 94, 358) obtained the *monohydrated hydroxide* $\text{ZnO} \cdot \text{H}_2 \cdot \text{H}_2\text{O}$ in very lustrous octahedra by keeping a saturated solution of the hydroxide in NaOHaq in a closed vessel for some weeks. S.G. of $\text{ZnO} \cdot \text{H}_2$ is given by Nickles (*l.c.*) as 2.677, and by Filhol (*A. Ch.* [5] 21, 415) as 3.053. Thomsen gives $[\text{Zn}(\text{O} \cdot \text{H})_2] = 82.680$ (*Th.* 3, 275). $\text{ZnO} \cdot \text{H}_2$ dissolves easily in acids, forming salts ZnX^+ .

$\text{ZnO} \cdot \text{H}_2$ also dissolves in caustic alkali solutions, and in $(\text{NH}_4)_2\text{CO}_3\text{aq}$. By adding alcohol to a solution of $\text{ZnO} \cdot \text{H}_2$ in KOHaq , Laux (*A.* 9, 183) obtained small lustrous crystals ($?\text{ZnO} \cdot \text{K}$); Fremy (*C. R.* 15, 1106) obtained ($?$) $\text{ZnO} \cdot \text{K}$, ZnO ; by using NaOHaq Come; & Jackson (*B.* 21, 1589 [1888]) obtained two compounds derived from $\text{ZnO} \cdot \text{H}_2$ by replacing H by Na . They shook a solution of $\text{ZnO} \cdot \text{H}_2$ in conc. NaOHaq with alcohol; separated the upper (alcoholic) layer and allowed it to crystallise, and treated the lower (watery) layer repeatedly with alcohol until it solidified. The crystals from the lower layer had the composition

$\text{Zn}_2\text{O}_2\text{Na}_2\text{H}_2 \cdot 17\text{H}_2\text{O}$ (= $\text{Zn}_2(\text{OH})_2(\text{ONa})_2 \cdot 17\text{H}_2\text{O}$), agreeing, except in water of crystallisation, with an ammonium compound described by Malaguti (*C. R.* 62, 413 [1866]); this compound melts at $c. 70^\circ$, rapidly absorbs CO_2 from the air, loses $12\text{H}_2\text{O}$ at 100° , is insol. in ether, and is decomposed by water, but not in presence of excess of NaOH , with formation of ZnO and a little $\text{ZnO} \cdot \text{H}_2$. The crystals from the upper layer had the composition

$22\text{ZnO} \cdot \text{NaH} \cdot 7\text{H}_2\text{O}$ (= $22\text{Zn}(\text{OH})_2(\text{ONa}) \cdot 7\text{H}_2\text{O}$), corresponding with the compound described by Fremy (*l.c.*); this compound forms white radiating needles, which do not melt at 300° ; it

absorbs CO_2 from the air more slowly than the other compound, is decomposed by alcohol or water, and does not lose H_2O until heated above 200° (v. *Am.* 11, 145 [1899]). C. a. J. failed to obtain compounds derived from ZnO_2H_2 by replacing H by NH_4 or Mg. Compounds of ZnO with BaO , CaO , and MgO are described by Bertrand (*C. R.* 115, 999); these compounds are of the forms $2\text{ZnO} \cdot \text{MO} \cdot x\text{H}_2\text{O}$.

Zinc iodide of, ZnI_2 . Formula probably molecular, from analogy of ZnCl_2 . Formed by heating together zinc and iodine, and subliming; also by digesting I with water and excess of zinc until the liquid is colourless and evaporating over H_2SO_4 (Rammelsberg, *P.* 43, 665). Crystallises in white octahedra; S.G. 4.696 (Bödeker); melts at $c. 446^\circ$ (Carnelley, *C. A.* 33, 278); and boils at $c. 624^\circ$ (C. a. Williams, v. Carnelley's *Melting- and Boiling-point Tables*, 1, 23). H.F. (ZnI_2) = 49,230; [ZnI_2 , Aq] = 60,540 (*Th.* 3, 275). Heated in air ZnI_2 gives off I, and ZnO remains. Kremers (*P.* 111, 61) gives the following data:—

S.G. ZnI_2 , Aq	P.c. ZnI_2	S.G. ZnI_2 , Aq	P.c. ZnI_2
1.2310	23.1	1.9746	63.5
1.5121	42.6	2.3976	76.0
1.7871	56.3		

Hot ZnI_2 Aq is said to dissolve zinc in contact with the air, and on filtering an oxyiodide is said to be deposited (Müller, *J. pr.* 26, 411). ZnI_2 Aq also dissolves I; Baup (*J. Ph.* 9, 37 [1823]) says enough I is dissolved to form ZnI_4 .

ZnI_2 combines with NH_3 . By allowing a solution of ZnI_2 in NH_4 Aq to evaporate, Rammelsberg (*P.* 48, 152) obtained lustrous, four-sided prisms of $\text{ZnI}_2 \cdot 4\text{NH}_3$, decomposed by water with production of ZnO. Various double compounds with other iodides have been described: $\text{ZnI}_2 \cdot 2\text{MI}$, where $\text{M} = \text{NH}_4$, K or Na (Rammelsberg, *l.c.*; also *P.* 43, 665); $\text{ZnI}_2 \cdot 2\text{CsI}$ and $\text{ZnI}_2 \cdot 3\text{CsI}$ (Wells a. Campbell, *Zeit. f. anorg. Chemie*, 5, 273); $2\text{ZnI}_2 \cdot \text{BaI}_2$ (*l.c.*); $\text{ZnI}_2 \cdot 2\text{BiI}_3$, 12aq (Linna, *P.* 111, 240).

Zinc nitride of, Zn_3N_2 . Obtained by Frankland (*Pr.* 8, 502) by heating zinc amide ($\text{Zn}(\text{NH}_2)_2$; v. p. 887) to low redness. A grey, pulverulent solid; unchanged by heating to redness out of contact with air; reacts violently with water to give ZnO , H_2 , and NH_3 .

Zinc nitroprusside of, v. vol. ii. p. 341.

Zinc oxides of. Besides the normal basic oxide ZnO, there seems to be another higher (? superoxide) of zinc.

Zinc oxide ZnO. Formula not certainly molecular.

Occurrence.—With oxides of Mn, and Fe, as red zinc ore and franklinite.

Formation.—1. By burning zinc in air or O_2 . By strongly heating ZnO_2H_2 , $\text{Zn}(\text{NO}_3)_2$, ZnCO_3 , or another salt of zinc with a volatilisable acid.

Preparation.—Pure ZnSO_4 , prepared as described under ZnO, Preparation (p. 883), is dissolved in water, and the solution is very slowly added to a boiling solution of pure Na_2CO_3 , containing rather less Na_2CO_3 than suffices to decompose all the ZnSO_4 . The pp. of basic zinc carbonates is washed by decantation with boiling water until the washings are free from carbonates

and sulphates; it is then dried, powdered, and heated either in a Hessian crucible, or better, in a flask of hard glass, until a portion taken from the middle dissolves, when cold, in acid without effervescence. The solid is now finely powdered, sifted through a fine sieve, again heated, and then rubbed up with water, and washed and dried. ZnO is prepared in crystals by heating ZnCl_2 to redness in steam (Daubrée, *C. R.* 39, 153); also by heating the amorphous oxide slowly in a stream of H (Regnault, *A. Ch.* [2] 62, 350; Deville, *A. Ch.* [3] 43, 277); also by heating the amorphous oxide to whiteness in a stream of O_2 (Sidot, *C. R.* 69, 202); also by heating $\text{Zn}(\text{NO}_3)_2$ to redness (Brügelmann, *W.* 4, 283).

Properties.—Slightly yellow, powdery solid; becomes darker yellow when heated, but recovers its original colour on cooling. S.G. 5.5 to 5.7 (v. Brügelmann, *B.* 13, 1741; Filhol, *A. Ch.* [8] 21, 415; Hierapath, *C. J.* 1, 45; Karsten, *S.* 65, 394). S.G. crystalline (at 15°) 5.782 (Brügelmann, *W.* 4, 286). ZnO crystallises in slightly yellow, lustrous, chemimorphous pyramids belonging to the hexagonal system (B., *l.c.*). Thomsen (*Th.* 3, 275) gives H.F. (ZnO) = 85,430. Richards a. Rogers (*Am.* 15, 567 [1893]) found that ZnO, prepared by heating $\text{Zn}(\text{NO}_3)_2$, gave off some gas when dissolved in dilute acids; the maximum amount of gas from 10 g. ZnO was 20 c.c.; the gas consisted chiefly of N, with a little O; the higher the temperature to which the $\text{Zn}(\text{NO}_3)_2$ had been heated the less was the quantity of gas obtained; but some N always came off, even from ZnO which had been heated to the softening temperature of porcelain. Moissay (*C. R.* 115, 1031 [1892]) states that ZnO volatilises readily when heated in an electric furnace, and condenses again in transparent crystals. ZnO is not decomposed at $c. 1750^\circ$ (Read, *C. J.* 65, 313 [1894]).

Reactions and Combinations.—1. ZnO is a basic oxide. It interacts with most acids to form salts ZnX ($\text{X} = 2\text{NO}_3$, SO_4 , $\frac{2}{3}\text{PO}_4$, &c.) and water. 2. With fairly conc. caustic soda or potash, salts are formed which are most simply regarded as derived from ZnO_2H_2 , with H replaced by Na or K (v. Zinc hydrosulphide, p. 889). 3. ZnO is reduced to Zn, with explosive violence, by heating with magnesium (v. Winkler, *B.* 23, 122). 4. Morse a. White (*Am.* 11, 258) heated a mixture of ZnO and zinc in an exhausted tube, and found that a deposit of ZnO formed in the front part of the tube. They suppose that some of the original ZnO is supposed by the combined action of heat and zinc, and that zinc and O exist together in the hot part of the tube, but combine in the cooler parts of the tube to form ZnO_2 . 5. Oxylchlorides, oxylbromides, and probably oxyliodides of zinc are formed by heating ZnO with zinc chloride, bromide, and iodide respectively. 6. ZnO is reduced to zinc by heating with carbon or in carbon monoxide. 7. ZnO does not directly interact with water; ZnO_2H_2 is produced by ppg. a zinc salt solution by an alkali (v. Zinc hydrosulphide, p. 889). 8. By heating ZnO with oxides of aluminium, chromium, and iron along with B_2O_3 in a pottery furnace until the B_2O_3 was volatilised, Ebelsman (*A. Ch.* [8] 32, 34) obtained the compounds $\text{ZnO} \cdot \text{Al}_2\text{O}_3$, $\text{ZnO} \cdot \text{Cr}_2\text{O}_3$, and $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$.

ZINC PEROXIDE. In 1818 Thénard (*A. Ch.* [2] 9, 56) obtained what he called 'deutoxide de zinc' by the action of H_2O_2 on gelatinous $\text{ZnO} \cdot \text{H}_2\text{O}$, and also by adding KOH to a solution of $\text{ZnO} \cdot \text{H}_2\text{O}$ in HCl to which H_2O_2 had been added. In 1884 Haas (*B.* 27, 2249) obtained a white, tasteless, neutral, gelatinous pp. by adding H_2O_2 to solutions of zinc salts and then adding NH_4Ac ; after washing and drying at 100° , the solids had approximately the compositions Zn_2O_3 and Zn_2O_4 . H. thinks it probable that the substances obtained by him were compounds of ZnO and ZnO_2 ; the formula $2\text{ZnO} \cdot 3\text{ZnO}_2$ agrees well with some of his analyses.

Zinc oxybromides of. Oxybromides of zinc are formed by heating solutions of ZnBr_2 with ZnO , and by partially ppg. ZnBr_2 by NH_4Ac . Several compounds have been described by André (*Bl.* [2] 39, 398 [1884]):

- (1) $\text{ZnBr}_2 \cdot 4\text{ZnO} \cdot 2\text{H}_2\text{O}$, $x = 10, 13$, and 19 ;
- (2) $\text{ZnBr}_2 \cdot 5\text{ZnO} \cdot 6\text{H}_2\text{O}$; (3) $\text{ZnBr}_2 \cdot 6\text{ZnO} \cdot 36\text{H}_2\text{O}$.

Zinc oxychlorides of. These compounds are formed by adding to ZnCl_2 a quantity of NH_4Ac less than sufficient for complete ppg.; also by boiling ZnCl_2 with ZnO , or with certain other metallic oxides. Schindler (*Mag. Pharm.* 36, 45) obtained $\text{ZnCl}_2 \cdot 3\text{ZnO} \cdot 4\text{H}_2\text{O}$ by boiling ZnCl_2 with ZnO and the same compound by partially ppg. ZnCl_2 by NH_4Ac . By adding to ZnCl_2 so much NH_4Ac that the pp. which formed at first partly dissolved, and also by treating $\text{ZnCl}_2 \cdot 4\text{NH}_3$ with water, Kane (*A. Ch.* 72, 296) obtained $\text{ZnCl}_2 \cdot 6\text{ZnO} \cdot 10\text{H}_2\text{O}$. André (*C. R.* 106, 854) obtained $2\text{ZnCl}_2 \cdot 3\text{ZnO} \cdot 11\text{H}_2\text{O}$ by boiling ZnCl_2 with HgO and letting the solution cool; using P^2 he obtained another oxychloride, probably $\text{ZnCl}_2 \cdot 3\text{ZnO}$, combined with $\text{ZnCl}_2 \cdot \text{PbO}$.

Zinc oxyiodides of. According to Müller (*J. pr.* 28, 441 [1842]), ZnI_2 dissolves zinc when warmed therewith in the air; on cooling, an oxyiodide, $\text{ZnI}_2 \cdot 3\text{ZnO} \cdot 2\text{aq}$, is ppg.

Zinc oxysulphides of. The compound $4\text{ZnS} \cdot \text{ZnO}$ occurs native as *voltzite*, as spherical globules in some specimens of *galena*. A compound having the same composition was found in a furnace due at Freiberg by Karsten (*S.* 57, 186). By heating dry ZnSO_4 to redness in H , Arfvedson obtained a yellow-coloured oxysulphide $\text{ZnS} \cdot \text{ZnO}$ (*P.* 1, 69).

Zinc perbromoplatinocyanide of. v. vol. ii. p. 845.

Zinc phosphides of. Zinc and P combine when heated together, forming a greyish, lustrous, somewhat malleable compound. By heating finely powdered zinc in vapour of P, Schrötter obtained a compound, with S.G. 4.76, having the composition Zn_3P_2 (*W. A. B.* 1359, 301). Vigier obtained the same compound by heating zinc in P , until distillation began, and then passing H laden with vapour of P over the zinc. The same compound was formed by Regnault (*A. Ch.* [4] 9, 162) by heating to whiteness a mixture of MgHPO_4 , ZnS and O ; along with the Zn_3P_2 were formed crystals of another phosphide, probably ZnP ; and by treating ZnP with dilute acid, an amorphous, yellow solid remained which detonated when mixed with KClO_4 and struck, and which was perhaps ZnP . The compound Zn_3P_2 was obtained by

Hogsfeld (*A.* 100, 99) by strongly heating a mixture of ZnO , P_2O_5 , and O . By heating a mixture of NaPO_3 and zinc shavings in a retort, H. (*loc.*) obtained a yellowish red, loose sublimate which contained Zn and P ; and by heating the fused mass in the retort with HCl , grey lustrous tablets of ZnP_2 remained. Lüpke (*C. O.* 1890 [ii.] 642) formed zinc phosphide (1 ZnP_2) by adding amorphous P to molten zinc covered with $(\text{NH}_4)_2\text{CO}_3$; this phosphide was not decomposed by water, but was slowly decomposed by dilute HCl , giving off PH_3 .

For the compound ZnP_2 v. **ZINC HYDROPHOSPHIDE**, p. 838.

Zinc, platincyanide of. v. vol. ii. p. 844.

Zinc, salts of. Many salts are obtained by replacing the H of acids by zinc. The greater number of the salts of zinc are normal salts; several basic carbonates, nitrates, and sulphates are known. The following are the chief salts of zinc derived from oxyacids:—*Argentite* and *arsenate*, *borate*, *bromate*, *carbonates*, *chlorate* and *perchlorate*, *chromates*, *iodate* and *periodates*, *molybdates*, *nitrates* and *nitrites*, *phosphates* and *phosphites*, *selenate* and *selenite*, *silicate*, *sulphates* and *sulphite*, *thiosulphate*, *tungstates*, *vanadates* (v. **CARBONATES**, **NITRATES**, **SULPHATES**, &c.).

Zinc, selenide of. ZnSe . This compound, is formed, in reddish-yellow, regular crystals, S.G. 5.40, by heating zinc to redness in a stream of H_2Se , and then subliming in a slow stream of H (Margottet, *C. R.* 84, 1293).

Zinc, selenocyanide of. v. vol. ii. p. 848.

Zinc, silicofluoride of. $\text{ZnSiF}_6 \cdot 6\text{H}_2\text{O}$. Obtained in hexagonal plates, easily sol. in water, by evaporating to a small bulk a solution of ZnO in H_2SiF_6 (Berzelius). S.G. 2.104 (Topsøe, *C. C.* 4, 76).

Zinc, stannifluoride of. $\text{ZnSnF}_6 \cdot 6\text{H}_2\text{O}$; v. this vol., p. 724.

Zinc, sulphocyanide of. v. vol. ii. p. 853.

Zinc, sulphide of. ZnS . This compound is not formed by heating together zinc and S, as the S volatilises before the temperature of combination is reached.

Occurrence.—As zinc blende.

Preparation.—1. By repeatedly subjecting a mixture of zinc and S, in the ratio $\text{Zn}:\text{S}$, to a great pressure; the product resembled zinc blende (Spring, *Z.* 16, 1,000).—2. By rapidly heating a mixture of zinc filings and cinnabar in a retort; formation of ZnS occurs with detonation; Hg distils off.—3. By heating ZnO with S.—4. By heating ZnO , or $\text{ZnO} \cdot \text{H}_2\text{O}$, in a stream of H_2S ; in the case of $\text{ZnO} \cdot \text{H}_2\text{O}$, formation of ZnS takes place very slowly (v. Wagner, *D. P. J.* 187, 334).—5. ZnS is also formed by heating dry ZnSO_4 with S and O .—6. ZnS is obtained by passing H_2S into a neutral or alkaline solution of a zinc salt, or into a solution in a weak acid, such as acetic acid, washing the pp., drying it at 100° , and heating in a stream of dry H_2S . The pp. dried at 100° is said to be $2\text{ZnS} \cdot \text{H}_2\text{O}$ (Geiger a. Reimann, *Mag. Pharm.* 31, 178; cf. Squibay, *Fr.* 7, 78).

Properties and Reactions.—**S.G.** of $\text{ZnS} = 3.93$ (Karsten, *S.* 65, 394); **S.G.** of *blende* = 4.03 to 4.07 (v. Neumann, *P.* 28, 1). Thomsen (*Zh.* 5, 276) gives H.F. of $\text{ZnS} \cdot \text{H}_2\text{O}$ as $[\text{ZnS} \cdot \text{H}_2\text{O}] = 41,680^\circ$. ZnS prepared by ppg. is a yellowish

solid; easily sol. in acids, forming salts of Zn and giving off H_2S . Zinc blende is a grey to black crystalline solid; slowly acted on by acids. By repeatedly washing ppd. ZnS , also by passing H_2S into water containing pure $ZnO \cdot H_2O$ in suspension, Winssinger (*Bt.* [2] 49, 452 (1888)) obtained colloidal ZnS , sol. in water; the solution could be boiled until all excess of H_2S was expelled without ppn. of ZnS . ZnS prepared by adding excess of NH_4Aq to $ZnCl_2Aq$, ppd. all the zinc as ZnS by H_2S , washing and drying the pp., and then heating nearly to whiteness in a Hessian crucible inside a plumbago crucible, is very phosphorescent (*v. Henry, C. R.* 115, 503).

By heating ZnS with zinc in a vacuum tube, Morse a. White (*Am. J.* 21, 348) found that some of the ZnS was carried forward and deposited on the cooler part of the tube; they supposed that some of the ZnS was decomposed, and that Zn and S existed in the hottest part of the tube and combined in the cooler portions. By heating blende with I and a little water some $ZnSO_4$ is formed (Filhol a. Melhies, *A. Ch.* [4] 22, 68; Lasaulx, *J.* 1870, 1272).

According to Schiff (*A.* 115, 74), a polysulphide of zinc, probably ZnS_3 , is formed by ppd. a neutral solution of a salt of zinc by K_2S_2Aq , and drying the pp. over H_2SO_4 . Spring (*B.* 16, 1000) thought that a polysulphide of zinc was probably formed by strongly compressing a mixture of zinc with excess of S.

Zinc, telluride of, $ZnTe$. Obtained, in large ruby-red, regular crystals, by strongly heating zinc in a stream of H_2Te , and then subliming in a slow current of H (Margottet, *C. R.* 84, 1293).

Zinc, titanifluoride of, $ZnTiF_6$; *v.* this vol., p. 742. M. M. P. M.

ZINC, ORGANIC COMPOUNDS OF.

Zinc methyl or Zinc methide $ZnCH_3$, *i.e.* $ZnMe$. Mol. w. 95. V.D. 3.29 (calc. 3.30). [-40°] (Haase, *B.* 26, 1053). (46°). S.G. 1.386.

Formation.—1. By heating methyl iodide with zinc in sealed tubes at 150° . The compound $IZnMe$ is formed as an intermediate product. The reaction takes place more easily when the MeI is mixed with two-thirds of its volume of ether and heated to 100° , but it is then difficult to separate the ether from the $ZnMe_2$ (Frankland, *A.* 85, 346; 111, 62; Wanklyn, *C. J.* 13, 124; Butlerow, *A.* 144, 2; Ladenburg, *A.* 173, 147).—2. By heating finely granulated zinc with $HgMe$, in a sealed tube for 24 hours, at 120° , and distilling the product (Frankland a. Duppa, *C. J.* 17, 30).—3. $IZnMe$ is formed in 24 hours if MeI is left in contact with a large amount of copper-zinc couple (Gladstone, *C. J.* 35, 109).

Preparation.—Zinc filings (9 pts.) are heated with reduced copper (1 pt.), till the copper-zinc couple is produced, and the product treated with MeI (Gladstone, *C. J.* 35, 569).

Properties.—Colourless mobile liquid, taking fire on exposure to air. Decomposed by water into CH_4 and $Zn(OH)_2$. By very careful oxidation it appears to yield $Zn(OMe)_2$, and crystalline $ZnMe(OMe)$, which is split up by water into $Zn(OH)_2$, methyl alcohol, and CH_4 .

Reactions.—1. *Acetyl chloride* (1 mol.) forms $CH_3.CCl(OZnMe).CH_3$, which is slowly converted, by further treatment with $ZnMe_2$, into

$CH_3.CMe(OZnMe).CH_3 + ClZnMe$, crystallising in prisms, and converted by water into *tert*-butyl alcohol, CH_3 , zinc chloride, and $Zn(OH)_2$. The compound $CH_3.CCl(OZnMe).CH_3$ yields acetone on addition of water (Butlerow, *Z.* 1864, 365, 702; Pawlow, *N. Petersb. Acad. Bull.* 22, 497; Bogomeletz, *A.* 209, 88).—2. *Bromoacetyl bromide*, followed by water, yields methyl-isopropyl carbinol (Winogradoff, *A.* 191, 127).—3. In ethereal solution *secondary hexyl iodide* has no action at 100° ; but at 125° the products appear to be CH_3 , ethyl iodide, and hexylene (Purdie, *C. J.* 39, 464).—4. *Chloral* followed by water forms $CCl_3.CHMe.OH$, while butyric chloral yields $CH_3Cl_2.CHMe.OH$.—5. *Nitric oxide* passed into $ZnMe$, forms $CH_3N_3O_2(ZnMe)$, which is decomposed by water, yielding crystalline $(CH_3N_3O_2)_2ZnAq$, from which the Na salt $CH_3N_3O_2NaAq$ of 'di-nitro-methyl' acid may be obtained (Frankland, *A.* 99, 360).

Zinc ethyl or Zinc ethide $ZnEt$. Mol. w. 123. [-28°] (Haase, *B.* 26, 1053). (118°). S.G. 1.182. H.F. -31,800 (Guntz, *C. R.* 105, 673). V.D. 4.26 (obs. and calc.).

Formation.—1. By heating zinc or zinc-sodium alloy with EtI or a mixture of EtI and ether (Frankland, *C. J.* 2, 297; 3, 44; *Tr.* 122, 431; 145, 259; *A.* 95, 28; Wanklyn, *C. J.* 13, 121; Pebal, *A.* 118, 22; 121, 105; Rieth a. Beilstein, *A.* 123, 245; 126, 248; Chapman, *Laboratory*, 1, 195; Alexojeff a. Beilstein, *C. R.* 63, 171; Rathke, *A.* 152, 230; Wichellhaus, *J.* 1868, 425).—2. By heating granulated zinc with $HgEt$, in sealed tubes for 36 hours at 100° (Frankland a. Duppa, *C. J.* 17, 3).—3. From zinc filings and $EtBr$ (Wichellhaus, *A.* 152, 321).

Preparation.—Clean zinc filings (180 g.) are mixed with copper (20 g.) reduced from the oxide at a dull-red heat by coal gas; the mixture is rapidly heated over a very large Bunsen flame, and is well shaken meanwhile. As soon as the filings begin to cake together and the copper is no longer visible, the copper-zinc couple has been made. The flask is now connected with an inverted condenser, inclined slightly upwards, and when it is cold ethyl iodide (175 g.) is added. Dry CO_2 is passed through the apparatus, and the flask heated by a water-bath; in half an hour the EtI ceases to run back from the condenser, for it has been converted into $IZnEt$. The apparatus is now tilted so that the condenser is inclined downwards, and heated in a bath of paraffin. The reaction $2IZnEt = ZnI_2 + ZgEt$, now takes place, and $ZnEt_2$ (60 g.) is collected in a receiver kept full of CO_2 (Gladstone a. Tribe, *C. J.* 26, 446; 35, 569).

Properties.—Colourless, mobile liquid, fuming in the air, and quickly taking fire, burning with a luminous green-edged flame, and giving off clouds of $ZnCl_2$. Immediately decomposed by water into $Zn(OH)_2$ and ethane. In like manner it attacks organic compounds containing hydroxyl or amidogen, with elimination of ethane. It causes india-rubber to swell remarkably.

Reactions.—1. Gradually treated with dry oxygen, it appears to produce $ZnEt(OEt)$ and $Zn(OEt)_2$, successively (Frankland). According to Demuth a. Meyer (*B.* 23, 894), the passage of oxygen through a solution of $ZnEt$ in ligroin

(7 vols.) yields EtZn.O.O.Et , which is decomposed by heat, sometimes with explosive violence. The compound EtZn.O.O.Et sets free I from a solution of KI and yields alcohol when distilled with dilute H_2SO_4 .—2. Sulphur forms zinc mercaptide Zn(SET)_2 . It appears to act in like manner (Chabrie, *Bl.* [3] 2, 788).—3. Iodine forms IZnEt and ZnI_2 successively, together with EtI . Bromine acts in like manner. Zinc ethyl takes fire in chlorine.—4. Dry ammonia forms $\text{Zn(NH}_3)_2$, and ethane (Frankland, *Pr.* 8, 502).—5. Nitric oxide is absorbed by an ethereal solution of ZnEt_2 , forming crystalline $\text{ZnEt}_2(\text{NO})_2$, which melts below 100° and is split up by water into ethane and $\text{C}_2\text{H}_5\text{N}_2\text{O}_2\text{ZnO.H}$. Carbon dioxide passed into an aqueous solution of this salt ppts. zinc carbonate, while zinc α -dinitroethylate ($\text{C}_2\text{H}_5\text{N}_2\text{O}_6$) $_2\text{Zn}$ remains in solution (Frankland, *Tr.* 1857, 59; *A.* 90, 342; *C. J.* 37, 570). The salt ($\text{C}_2\text{H}_5\text{N}_2\text{O}_6$) $_2\text{Zn}$ aq. crystallises in prisms, yields NH_3 and NH_4Et on treatment with sodium-amalgam (Zuckschwerdt, *A.* 174, 302), and HNO_3 and NH_4Et on treatment with alcoholic potash (Zorn, *B.* 15, 1008). The dinitroethylates NaA , BaA , CaA , ZnA , MgA , CuA , AgA , and $\text{AgA}(\text{NO}_3)$ were prepared by Frankland.—6. SO_2 forms zinc ethane sulphinate (Hobson, *C. J.* 10, 456).—7. PCl_5 yields PEt_3 (Hofmann a. Cahours, *Tr.* 1857, 578).—8. SiCl_4 gives SiEt_4 .—9. Heated with EtI at 170° it forms n -butane and ZnI_2 . Ethane and ethylene are also formed (Brodie, *C. J.* 3, 405). ZnEt_2 does not act on amyliodic.—10. Displaces halogens in organic compounds by ethyl.—11. Adds itself to a carbonyl group. Thus with *di-n-propyl ketone* it forms $\text{Et}_2\text{C(OZnEt)}_2$, which is converted by water into tri-ethyl carbinol. *Di-n-propyl ketone* forms, in like manner, ethyl-di-propyl carbinol. Ketones containing the group CO.CH_3 act differently, forming condensation-products; thus acetone yields mesityl oxide and phorone (A. Saytzeff, *J. pr.* [2] 31, 319). Zinc ethyl has no action on paraldehyde (Wedensky, *J. pr.* [2] 39, 568). With acetic aldehyde it forms $\text{CH}_3\text{CH(OZnEt).OZnEt}$, which is converted by water into *sec*-butyl alcohol.—12. In some cases it can add ZnEt_2 and H to a carbonyl group, C_2H_5 being evolved. Thus ZnEt_2 converts chloral, dissolved in pure ether, into crystalline $\text{CCl}_3\text{CH}_2\text{OZnEt}$, which is converted by water into tri-chloro-ethyl alcohol (Delacere, *Bl.* [2] 48, 784). Further action of zinc ethide on chloral yields $(\text{CCl}_3\text{CH}_2\text{O})_2\text{Zn}$, a white powder. In like manner butyric chloral is converted into $\text{C}_4\text{H}_9\text{Cl}_3\text{CH}_2\text{O.H}$. In this splitting off of Zn olefine, ZnEt_2 differs from ZnMe_2 , but resembles zinc propyl and zinc isobutyl (Garzaroli, *A.* 225, 102).—13. Can displace oxygen by two ethyl radicals; thus it converts *oxalic ether* into $\text{CO}_2\text{Et.CEt.CO}_2\text{Et}$ (Frankland a. Duppa, *A.* 142, 1; *P.* 12, 396).—14. Can displace ethoxyl by ethyl. Thus it converts *formic ether* into HCEt(OZnEt).OEt and then into HOEt(OZnEt).Et , which is turned by water into di-ethyl carbinol (Wagner a. Saytzeff, *A.* 175, 851).—15. Can displace chlorine by hydrogen. Thus with *chloro-benzoic acid* the first product is probably $\text{C}_6\text{H}_4(\text{ZnEt).CO}_2\text{Et}$, which is converted by water into benzoic ether, C_6H_5 , and ZnO .—16. With *benzonitrile* at 150° , and subsequent treatment with alcohol, cyanophenol is formed (Frankland a. Evans, *C. J.* 37, 568). It

polymerises phenyl-acetonitrile in the same way, forming cyanobenzene.—17. Cyanogen forms ZnCy_2 , and EtCN (Frankland a. Graham, *C. J.* 37, 740).—18. *Acetobenzene* is reduced by ZnEt_2 , followed by water, to aniline (Frankland a. Louis, *C. J.* 37, 563).—19. Acts on primary and secondary amines, giving off ethane, but has no action on tertiary amines (Frankland, *Pr.* 8, 502; *Gal. J. Ph.* [5] 7, 484). ZnEt_2 has no action on nicotine or quinoline, but forms with many alkaloids containing O compounds from which the alkaloids are regenerated by water.—20. *Acetamide* gives $(\text{AcNH})_2\text{Zn}$, while oxamide gives $\text{C}_2\text{O}_2(\text{NH})_2\text{Zn}$.—21. Acts on HgCl_2 , forming CHgEt and HgEt_2 (Buckton, *A.* 109, 218). HgCl_2 yields HgEt_2 , mercury, and ZnCl_2 .—22. AgCl forms ZnCl_2 , silver, and butane.—23. CCl_4 forms EtCl , ethylene, and propylene (Rieth a. Beilstein, *A.* 124, 242).—24. *Chloroform* yields amylene (H. a. B.), while bromoform gives propylene and EtBr (Alexejeff a. Beilstein, *C. R.* 58, 172). CHCl_3 produces ethylene, butane, and hydrogen (Borodine, *A.* 126, 239).

Zinc bromo-ethylide ZnBrEt . [62°]. Formed by the action of the copper-zinc couple on EtBr at 100° (Gladstone a. Tribe, *C. J.* 27, 410). Pearly scales, decomposed by heat partly into ZnBr_2 and ZnEt_2 , and partly into Zn , ZnBr_2 , C_2H_4 , and C_2H_6 .

Zinc iodo-ethylide ZnIEt . Formed in like manner. Crystalline. Split up by heat into ZnI_2 and ZnEt_2 .

Zinc propyl ZnPr . (148°) (S.); (146°) (Gladstone a. Tribe, *B.* 6, 1136); (150°) (Pape, *B.* 14, 1873). Formed by heating propyl iodide with zinc and a small quantity of an alloy of zinc and sodium (Steherbakoff, *Bl.* [2] 37, 345). Heavy liquid, with disagreeable odour. Reacts with aldehydes, forming propylene and such compounds as RCH_2OZnPr , which yield secondary alcohols on addition of water.

Zinc isopropyl ZnPr . (136°) with decomposition; (96° at 40 mm.). Got by heating PrI (170 g.) with ether (100 g.), zinc (100 g.), and zinc-sodium (3 g.) at 100° (Ragozin, *J. R.* 24, 549). Fuming liquid. Yields crystalline Zn(OPr) , on exposure to air. Split up at 132° into Zn and hydrocarbons (Gladstone a. Tribe, *C. J.* 39, 6).

Zinc isobutyl $\text{Zn(C}_4\text{H}_9)_2$. (166°) at 734 mm. (Garzaroli-Thurnlackh a. Popper, *A.* 223, 167). Formed from zinc and $\text{Pr.CH}_3\text{I}$. Got also from Zn and $\text{Hg(C}_4\text{H}_9)_2$ (Cahours, *Bl.* [2] 21, 357).

Zinc isocamyl $\text{Zn(C}_5\text{H}_{11})_2$. (220°). S.G. 1.022. V.D. 6.95 (calc. 6.87). Prepared by heating zinc with $\text{Hg(C}_5\text{H}_{11})_2$ (Frankland, *A.* 85, 360; 130, 122). Liquid, fuming in the air but not taking fire. Takes fire in oxygen. When added to cooled aldehyde it yields, after addition of ice-cold water, methyl-isocamyl-carbinol, isopropyl-ethylene, and ethyl and isocamyl alcohols (Sokoloff, *C. C.* 1587, 988).

ZINCATES. Compounds derived from ZnO.H_2 by replacing H by positive metals; v. ZINC HYDROXIDES, p. 888.

* ZERCONATES v. under ZINCONIUM HYDROXIDE, p. 896.

ZINCONIUM. *oxide of zinc* (v. p. 886). ZnZnCONIUM . *Zr.* At. w. 69.0 (v. p. 894). Mol. w. not known. Melts above m.p. of Si (i.e. above $c. 1300^\circ$) (Troost, *J.* 1865, 188). S.G. 4.16 (Troost, *Lo.*); 4.25 (Moissan, *C. R.* 116,

1722). S.H. (0°-100°) -065 (Mixer a. Dana, *M.* 169, 388 [1873]).

Historical.—Klaproth in 1789 (*Beiträge*, 1, 208, 227) announced the discovery of a new earth, in combination with silica, as the rare mineral *zircon*. The same earth has been found in a few other rare minerals, such as *eudialyte*, *polyphignite*, *ferrysomite*, &c. Bright-coloured varieties of zircon are generally called *hyacinth*, the greyish or brown kinds are called *zirconite*, and a variety which is nearly colourless is known as *jargon*.

In 1845 Svanberg (*A.* 56, 223) stated that zirconia was a mixture of at least three oxides, but Berlin (*J. pr.* 58, 147), Marignac (*A. Ch.* [3] 60, 267), and Hermann (*J. pr.* 31, 75; 97, 331) failed to obtain any evidence of the composite character of zirconia. At a later time, Sorby (*B.* 2, 126, 193 [1869]), and also Forbes (*B.* 2, 337, 383), thought they had obtained spectroscopic indications of the presence of another earth in *zircon*; but it was shown that the abnormalities observed were due to traces of compounds of uranium (Sorby, *C. N.* 21, 73; Knop, *A.* 159, 44; cf. Hannay, *C. J.* 26, 703).

Occurrence.—Never uncombined. The principal naturally occurring compound of Zr is *zirconite*, which is more or less pure $ZrSiO_4$. This mineral is found in small quantities in the sand and alluvial deposits of certain rivers in Ceylon, and in the older rocks in many parts of the world; it has been found in the granites of Sweden, Switzerland, Tyrol, and North America (*v. J. M.* 1877, 97).

Formation.—1. By heating K_2ZrF_6 with K (Berzelius, *P.* 4, 117 [1825]).—2. By passing vapour of ZrF_4 over Na in a red-hot tube (Troost, *C. R.* 61, 109 [1865]).—3. By heating ZrO_2 with Mg (Phipson, *J. pr.* 96, 353 [1865]).—4. By melting ZrO_2 in a carbon crucible in an electric furnace; or by mixing ZrO_2 with carbon, melting in an electric furnace, then mixing the Zr carbides thus formed (*v. Carbides*, p. 894) with excess of ZrO_2 and again melting (Moissan, *C. R.* 116, 1222 [1893]).

Preparation.—1. Finely powdered *zirconite* ($ZrO_2 \cdot SiO_2$) is thoroughly mixed with an excess of finely powdered carbon, the mixture is compressed into small cylinders which are placed in a closed carbon crucible and heated in an electric furnace (with a current of 30 to 35 amperes and 70 volts), while a stream of CO_2 is sent through the crucible; the greater part of the SiO_2 is thus volatilised (Troost, *C. R.* 116, 1428). The carbides of Zr in the crucible are now mixed with excess of ZrO_2 and melted in the electric furnace (Moissan, *C. R.* 116, 1222).—2. Finely powdered and sifted *zirconite* is mixed with 2 to 3 lime its weight of KHF_4 , the mixture is heated to bright redness for c. 15 mins., and, after cooling, is boiled with water containing a little dilute $HFAg$; K_2SiF_6 is removed by filtration, the filtrate deposits K_2ZrF_6 on cooling. The K_2ZrF_6 is re-crystallised from water, then dried, mixed with K, and heated in a vessel of glass or iron; the product is washed with water, digested for a long time with conc. $HClAq$ at 40°, then washed with water containing NH_4Cl , and finally with alcohol (Berzelius, *Lc.*; Troost, *A.* 136, 353). This method yields *amorphous zirconium*. According to Bailey (*Pr.* 46, 74 [1899]), the only

method that gives nearly pure amorphous Zr is to heat ZrO_2 with Mg foil (not powder) and treat with $HClAq$.—3. One part dry K_2ZrF_6 is mixed with 1½ pts. Al, and the mixture is heated to the melting-point of iron in a crucible made of gas coke; the product is digested with conc. $HClAq$ diluted with twice its volume of water, when the crystalline leaflets of Zr, that have formed on the surface of the Al, separate from the mass of Al before the latter is wholly dissolved. When the whole of the Al has dissolved an alloy of Zr and Al remains, besides the crystalline leaflets of Zr; if the temperature of reduction is not sufficiently high, the main product is the Zr-Al alloy (Troost, *Lc.*; cf. Franz, *B.* 8, 58). This method yields *crystalline zirconium*.

Various methods have been used for decomposing *zirconite* and obtaining compounds of Zr. Franz (*B.* 3, 58) fuses the powdered mineral with $KHSO_4$, treats the fused material with boiling water containing a little H_2SO_4 , washes the insoluble $3ZrO_2 \cdot SO_3$ thus formed, and adds it, in small portions at a time, to molten $NaOH$; he then lixivates with cold water, dissolves the ZrO_2 that remains in hot conc. H_2SO_4 , dilutes, pptts. by NH_4Aq , washes, dries, and decomposes the $ZrO_2 \cdot xH_2O$ by heat. The method of fusing with KHF_4 used by Marignac (*v. supra*, No. 2) yields pure K_2ZrF_6 very readily; $Zr(SO_4)_2$ may be obtained by heating the K_2ZrF_6 with conc. H_2SO_4 (*v.* Hiortdahl, *A.* 137, 34; cf. *J. pr.* 88, 201). For other methods *v.* Hermann (*J. pr.* 97, 330); Scheerer (*P.* 59, 48); Stromeyer (*A.* 113, 727); Chancel (*J. pr.* 74, 471); Berlin (*J. pr.* 58, 145); Henneberg (*J. pr.* 38, 508); Bailey (*Pr.* 46, 74 [1899]).

Properties.—Zirconium has been isolated as black amorphous powder, and also as a greyish crystalline solid.

Amorphous zirconium (*v. Preparation*, No. 2) is a black powder, which is extremely porous and resembles powdered charcoal; when pressed with a burnisher it agglomerates to graphite-like laminae. After being heated strongly, and then cooled, *in vacuo*, it is said to glow and burn when exposed to air. The porous amorphous metal is said not to conduct electricity. Amorphous Zr is stated to be insoluble in ordinary acids, including *aqua regia*; but, according to Bailey (*Pr.* 46, 74 [1899]), it dissolves in cold conc. H_2SO_4 ; $HFAg$ dissolves it readily, H being given off. It is oxidised by heating in the air, when it burns to ZrO_2 with a brilliant white light; oxidation is also effected by fusion with caustic or carbonated alkalis, or with KNO_3 or $KClO_4$.

Crystalline zirconium (*v. Preparation*, No. 3) is a very lustrous, greyish, brittle, solid, which resembles Sb in appearance; very hard, easily scratching glass and ruby (Moissan, *C. R.* 116, 1222). S.H. 4.15 (Troost, *J.* 1865, 188; 4.26 (Moissan, *Lc.*). S.H. (0° to 100°) -066 (Mixer a. Dana, *A.* 169, 388 [1873]). Crystalline Zr burns in the $O-H$ flame; it is not oxidised in O until heated to whiteness; it dissolves slowly in hot conc. $HClAq$, and is very slightly acted on by HNO_3Aq or H_2SO_4 , even when warm; cold $HFAg$ dissolves it readily. Molten $KClO_4$, or KNO_3 , is said to be without action; molten KOH dissolves the metal as long as any moisture is present.

According to Troost (*J.* 1865, 188), Zr melts above the m.p. of Si (i.e. above c. 1800°). The emission-spectrum of Zr has been mapped by Thalén; the chief lines are 6127 in the red, and in the blue, 4815, 4771, 4788, 4709, and 4686.

The at. w. of Zr was determined, (1) by Berzelius (*P.* 4, 126; 8, 186, [1825]), by finding the ratio of ZrO_2 to SO_2 in the sulphate; (2) by Hermann (*J. pr.* 81, 77 [1844]) by analysing $ZrCl_2$; (3) by Marignac (*A. Ch.* [3] 80, 270 [1860]), by analysing K_2ZrF_6 ; (4) by Bailey (*Pr.* 46, 74 [1889]), by decomposing $Zr(SO_4)_2$ by heat and weighing the ZrO_2 produced; (5) by Mixter & Dana (*A.* 169, 888 [1873]), by determining the S.H. of Zr; (6) by Deville & Troost (*P.* 108, 636; 641 [1859]), by determining the V.D. of $ZrCl_4$. The results of Berzelius gave the at. w. of Zr as 89.2; those of Hermann, 88.5 to 90.7; those of Marignac, 90.3 to 90.6; and the results obtained by Bailey gave 90.4 as the at. w. of the metal.

Zirconium is the third member of the even-series family of Group IV. in the periodic classification of the elements. This group contains the following elements:—

Even Series	2	4	6	8	10	12
	C	Ti	Zr	- Co	-	Th
Odd Series	3	5	7	9	11	
	Ni	Ge	Sn	-	Pb	

As is to be expected from its position in the classificatory system, Zr is a metal with some non-metallic properties; the oxide ZrO_2 forms corresponding salts, many of which are basic salts; the haloid compounds, ZrX_4 , are probably all volatilisable without decomposition (the V.D. of $ZrCl_4$ only has been determined), but aqueous solutions yield oxyhalides on evaporation; hydrated ZrO_2 reacts as a weak acid towards strong bases, forming zirconates; salts are known derived from the acid H_2ZrF_6 ; there is an oxide higher than ZrO_2 , probably ZrO_3 . For a more detailed comparison of Zr with the other even-series elements of Group IV. v. TITANIUM GROUP OF ELEMENTS (this vol. p. 749), and cf. TIN GROUP OF ELEMENTS (this vol. p. 735). The atom of Zr is tetravalent in the gaseous molecule $ZrCl_4$.

Reactions and Combinations.—1. Heated in air, or oxygen, Zr burns to ZrO_2 , giving out dazzlingly white light; amorphous Zr burns easily, crystalline only at a white heat, and then merely superficially.—2. Both amorphous and crystalline Zr dissolve readily in *hydrofluoric acid*, giving off H_2 and forming ZrF_4 .—3. According to Bailey (*Pr.* 46, 74), amorphous Zr dissolves in cold conc. *sulphuric acid*. Both forms dissolve in *aqua regia*.—4. Conc. *hydrochloric acid* reacts with Zr, when warm, forming $ZrCl_4$ solution. Crystalline Zr is said to interact with *gaseous hydrogen chloride*, at dull redness, forming $ZrCl_4$.—5. Amorphous Zr is oxidised by *molten potash* or *soda*, also by *molten nitre* or *potassium chlorate*; the crystalline form of Zr is said not to be acted on by molten KNO_3 or $KClO_3$, and by molten caustic alkalis only as long as there are traces of moisture present.—6. Zr combines directly with the *halogens*, to form ZrX_4 , and probably with *sulphur* (v. *Sulphide*, p. 897).

Detection and Estimation.—Addition of hot

edg. K_2SO_4 to solutions of salts of Zr ppt. white basic sulphate of Zr, which is insoluble in water and nearly insoluble in much $HClAq$. Turmeric paper becomes reddish-brown when immersed in a solution of a salt of Zr in $HClAq$; the reaction is completely masked by the presence of boric acid (v. Brush, *J. pr.* 62, 7). Bailey (*C. J.* 49, 481 [1886]) found that addition of H_2O_2Aq to a slightly acid solution containing salts of Zr, along with salts of Fe, Nb, and Ti, ppt. the whole of the Zr as ZrO_2 (or Zr_2O_3), but none of the other metals. Troost makes use of the comparatively small volatility of ZrO_2 at a very high temperature, to separate this oxide from SiO_2 (v. *C. R.* 116, 1428).

Zr is generally estimated as ZrO_2 ; salts of volatilisable acids are decomposed by heat; or solutions may be ppt. by NH_4Aq and the pp. washed, dried, and strongly heated.

Zirconium, alloys of. An alloy of Zr with aluminium is obtained in the preparation of Zr by reducing K_2ZrF_6 by Al (v. *Preparation of Zirconium*, No. 3). Mellis (*Z.* [2] 6, 296) obtained crystals having the composition $ZrAl_3$ (or perhaps Zr_2Al_3Si) by heating to whiteness a mixture of 1 pt. powdered *zirconite* with 5 pts. *cryolite* powder, 10 pts. mixed KCl and $NaCl$, and 1 pt. Al, treating with dilute $HClAq$, and separating the larger crystals of the alloy from the finer crystals of Si.

Zirconium, bromide of, $ZrBr_4$. Formula probably molecular, from analogy of $ZrCl_4$. Obtained by mixing finely powdered Zr, with sugar charcoal, making into balls with starch paste, drying, and heating to bright redness in a current of dry CO_2 and dry Br (Mellis, *Z.* [2] 6, 296). $ZrBr_4$ is a white, microscopically crystalline, hygroscopic powder; it is easily volatilised; heated in H it is not reduced to a lower bromide. Contact with moist air or water produces the oxybromide $ZrOBr_2$; evaporation of an aqueous solution gives the heptahydrate of this compound $ZnOBr_2 \cdot 7H_2O$ in large needle-shaped, transparent crystals (M., l.c.).

Zirconium, carbides of. By heating an intimate mixture of ZrO_2 and C in the electric arc, in an atmosphere of CO_2 , Troost (*C. R.* 116, 1227 [1893]) obtained a very hard, steel-grey solid, approximating closely to the composition ZrC . By using less C, other carbides seem to be produced (cf. Moissan, *C. R.* 116, 1222), but analyses of other compounds are not given. ZrC dissolves easily in dilute $HFAq$, but is not acted on by other acids. Moissan (l.c.) says that carbides of Zr containing more than 5 p.c. C (ZrC contains c. 21 p.c. C) take fire fairly easily when exposed to the air; Troost says that carbides with a small proportion of C are only superficially oxidised by heating to redness, but that those with much C burn brilliantly at this temperature.

Zirconium, chloride of, $ZrCl_4$. Mol. w. c. 231.5. V.D. 117 at 440° (Deville & Troost, *P.* 108, 636).

Formation.—1. By heating Zr in Cl_2 .—2. By heating an intimate mixture of ZrO_2 and C in Cl_2 .—3. By passing vapour of $SiCl_4$ over heated ZrO_2 (Troost & Hautefeuille, *C. R.* 76, 1819).

Preparation.—A mixture of ZrO_2 with c. its own weight of lampblack is made into a paste with oil & little balls, c. the size of hazel-nuts.

are formed on this, and these are covered with powdered charcoal, and heated to full redness in a closed crucible until the oil is completely charred; the pellets are then heated to bright redness in a tube of hard glass, while a current of dry Cl is passed through the tube; the ZrCl₄ which forms on the cooler parts of the tube is drawn out into bulbs, which are sealed off when the operation is finished (v. Bailey, *Pr.* 46, 74).

Properties, Reactions, and Combinations.—A white solid; volatilises unchanged at c. 400°. Dissolves in water, with production of heat; the solution on evaporation gives *corychlorides* (q. v.). Does not interact with *silicic ethide* at 180° (Hinsberg, *A.* 239, 253). Combines with ammonia to form $\text{ZrCl}_4 \cdot \text{NH}_3$; with sodium chloride to form $\text{ZrCl}_4 \cdot 2\text{NaCl}$ (Paykull, *B.* 6, 1467).

Zirconium, ferrocyanide of. According to Hornberger (*A.* 181, 232), the pp. formed by adding $\text{K}_4\text{FeCy}_6\text{Aq}$ to a solution of a salt of Zr, when washed and dried, has the composition $\text{Zr}_2(\text{FeCy}_6)_2$ (?); it is a blue powder with a greenish tinge, insoluble in water, decomposed by acids, giving off HCN.

Zirconium, fluoride of, ZrF_4 . Formula probably molecular, from analogy of ZrCl_4 .

Formation.—1. The hydrated compound $\text{ZrF}_3 \cdot 3\text{aq}$ is formed by slowly evaporating a solution of $\text{ZrO}_2 \cdot \text{H}_2\text{O}$ or ZrF_4 in HFAq .—2. By heating ZrO_2 with twice its weight of $(\text{NH}_4)\text{HF}_2$ to dull redness, till all the ammonium salt is volatilised (Marignac, *A. Ch.* [3] 60, 263).

Preparation.—Deville (*A. Ch.* [3] 49, 84) obtained ZrF_4 by heating to whiteness a mixture of finely powdered *zirconite* and *fluorspar* in a stream of HCl ($7\text{ZrSiO}_4 + 2\text{CaF}_2 + 2\text{HCl} = \text{ZrF}_4 + \text{CaCl}_2 + \text{CaSiO}_3 + \text{H}_2\text{O}$).

Properties and Reactions.—Prepared as described, ZrF_4 is a colourless, transparent, crystalline (probably hexagonal) solid; volatilisable at white heat; insoluble in water and acids. ZrF_4 , prepared by heating ZrO_2 with $(\text{NH}_4)\text{HF}_2$ is said to be soluble in water and in dilute HFAq . The crystals of $\text{ZrF}_4 \cdot 3\text{aq}$ are partially decomposed on drying. Heated to full redness in air, ZrF_4 gives ZrO_2 and HF.

Combinations.—1. With water (v. *Formation*, No. 1) to form $\text{ZrF}_4 \cdot 3\text{aq}$.—2. With various metallic fluorides to form compounds of the form $\text{ZrF}_4 \cdot x\text{MF}_y \cdot \text{H}_2\text{O}$. These salts are often called *zircono-fluorides*, or *fluo-zirconates*; they are better named *zirconio-fluorides*. The *zircono-fluorides* have been examined chiefly by Marignac (*A. Ch.* [3] 60, 267); they are obtained either by gradual evaporation of solutions containing the constituent fluorides or by adding hydroxides or carbonates of the various metals to solutions of ZrF_4 in HFAq , and evaporating.

Ammonium zirconio-fluorides. Two salts are described: (1) $2\text{NH}_4\text{F} \cdot \text{ZrF}_4 = (\text{NH}_4)_2\text{ZrF}_6$, rhombic crystals, isomorphous with K_2ZrF_6 ; (2) $8\text{NH}_4\text{F} \cdot \text{ZrF}_4$, small octahedra showing simple refraction (Baker, *C. J.* 35, 763).

Cadmium zirconio-fluorides. Two salts seem to exist: (1) $2\text{CdF}_2 \cdot \text{ZrF}_4 \cdot 6\text{aq}$, monoclinic crystals, isomorphous with the Mn salts; (2) $\text{CdF}_2 \cdot 2\text{ZrF}_4 \cdot 6\text{aq}$, laminar, fan-shaped groups of crystals.

Manganese zirconio-fluorides. (1) $\text{MnF}_2 \cdot \text{ZrF}_4 \cdot 6\text{aq}$; and (2) $2\text{MnF}_2 \cdot \text{ZrF}_4 \cdot 6\text{aq}$.

Nickel zirconio-fluorides.

(1) $\text{NiF}_2 \cdot \text{ZrF}_4 \cdot 6\text{aq}$, hexagonal prisms; S.G. 2-237 (Topsøe, *C. C.* 4, 76); and (2) $2\text{NiF}_2 \cdot \text{ZrF}_4 \cdot 12\text{aq}$, monoclinic crystals. The first salt forms a double salt with K_2ZrF_6 , viz. $\text{NiZrF}_6 \cdot \text{K}_2\text{ZrF}_6 \cdot 8\text{aq}$.

Potassium zirconio-fluorides.

(1) K_2ZrF_6 ; obtained by strongly heating *zirconite* with two or three times its weight of KHF_4 , boiling with very dilute HFAq , filtering from K_2SiF_6 , and allowing the filtrate to cool. Crystallises in rhombic crystals, terminated by six-sided pyramids; solubility = 78 at 2°, 1-4 at 15°, 2-7 at 100° and 25 at 100°. S.G. 3-582 (Topsøe, *L.c.*); (2) $\text{KF} \cdot \text{ZrF}_4 \cdot \text{aq}$ (= $\text{KZrF}_6 \cdot \text{aq}$); obtained, in monoclinic crystals, by dissolving the preceding salt in water containing a large excess of ZrF_4 ; (3) $3\text{KF} \cdot \text{ZrF}_4$ (= K_3ZrF_9); obtained by crystallising K_2ZrF_6 from a solution containing excess of KF; small, brilliant, regular octahedra, with simple refraction (v. Baker, *C. J.* 35, 762). Soluble in water; the hot conc. solution deposits K_2ZrF_6 on cooling.

Sodium zirconio-fluorides. The salt $5\text{NaF} \cdot 2\text{ZrF}_4$ is said to be always formed in whatever proportion the constituent fluorides are mixed. Small, monoclinic crystals; solubility at 18° = 38, and at 100° = c. 1-6.

Zinc zirconio-fluorides. (1) $\text{ZnZrF}_6 \cdot 6\text{aq}$; isomorphous with $\text{ZnSiF}_6 \cdot 6\text{aq}$ and $\text{ZnSnF}_6 \cdot 6\text{aq}$, crystallising in regular hexagonal prisms, easily soluble in water. S.G. 2-255 (Topsøe, *L.c.*). (2) $2\text{ZnF}_2 \cdot \text{ZrF}_4 \cdot 12\text{aq}$; deposited from a solution containing excess of ZnF_2 in monoclinic crystals, isomorphous with $2\text{NiF}_2 \cdot \text{ZrF}_4 \cdot 12\text{aq}$.

Zirconium, hydride of. By heating ZrO_2 and Mg powder, in the ratio $\text{ZrO}_2 \cdot 2\text{Mg}$, in an atmosphere of H, Winkler (*B.* 24, 898; cf. *B.* 23, 2666) obtained a black powder which burnt in O, and contained c. 73 p.c. H. On treating this with dilute HClAq , Mg and MgO dissolved, H being given off, and a black residue was left which W. regarded as ZrH_2 . Supposing the reduction of the ZrO_2 had proceeded in accordance with the equation $\text{ZrO}_2 + 2\text{Mg} + 2\text{H} = 2\text{MgO} + 2\text{ZrH}_2$, the product would have contained 53-44 p.c. ZrH_2 , and, therefore, would have given 1-15 p.c. H; as only 78 p.c. H was found, W. concluded that c. $\frac{1}{3}$ of the ZrO_2 had been reduced.

Zirconium, hydroxide of, (?) $\text{ZrO}_2 \cdot \text{H}_2\text{O}$. Addition of NH_4Aq to a solution of a salt of Zr produces a white, bulky, gelatinous pp. of $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$. According to Berzelius, the dry pp. has the composition $\text{ZrO}_2 \cdot \text{H}_2\text{O} = \text{ZrO}_2 \cdot \text{H}_2\text{O}$; Hermann (*J. pr.* 97, 318) gave the formula $\text{ZrO}_2 \cdot 2\text{H}_2\text{O} = \text{ZrO}_2 \cdot \text{H}_2\text{O}$, to the pp. dried at 17-5°; Paykull (*B.* 12, 1718) said that after drying *in vacuo*, the composition was $\text{ZrO}_2 \cdot 3\text{H}_2\text{O}$, and after drying at 100° $\text{ZrO}_2 \cdot \text{H}_2\text{O}$. A detailed examination of the dehydration of the pp. formed by adding NH_4Aq to a cold solution of $\text{Zr(NO}_3)_4$ was made by Carnelley a. Walker (*C. J.* 53, 68, 82 (1888)). The loss of water by the air-dried pp. was fairly regular to c. 90°, when the pp. had approximately the composition $\text{ZrO}_2 \cdot 2\text{H}_2\text{O}$; the loss was then less rapid, but very regular, up to c. 885°, whereat the composition was approximately $2\text{ZrO}_2 \cdot \text{H}_2\text{O}$; somewhere between 885° and 415° there was a sudden increase in the percentage loss of water.

for a rise of 10° , this increase being accompanied by a change of colour from grey to pure white; at 415° the composition was approximately $24\text{ZrO}_2 \cdot \text{H}_2\text{O}$; water was then given off very regularly, until at c. 560° dehydration was completed. C. a. W. conclude that probably no definite hydrate of ZrO_2 , unchanged throughout a fair range of temperature, is formed by heating $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ ppd. from a salt of Zr; they think that the change of colour which accompanies the comparatively large percentage loss of water at c. 400° is an accompaniment of a condensation of molecules chiefly of the composition $n(2\text{ZrO}_2 \cdot \text{H}_2\text{O})$ to molecules chiefly of the composition $n(24\text{ZrO}_2 \cdot \text{H}_2\text{O})$. There is a distinct resemblance between the phenomena of the dehydration of $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ and those of the dehydration of $\text{SiO}_2 \cdot x\text{H}_2\text{O}$, $\text{SfO}_2 \cdot x\text{H}_2\text{O}$, and $\text{TiO}_2 \cdot x\text{H}_2\text{O}$.

Hydrated ZrO_2 ppd. cold, and washed with cold water, dissolves easily in the ordinary acids, including oxalic acid (Bailey, C. 7, 49, 481), forming salts ZrX^+ , and ZrX^{++} ; when ppd. hot, or washed with hot water, the pp. is only slowly dissolved by the ordinary acids. According to Paykull (B. 12, 1719), moist $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ absorbs SO_2 from the air. Digestion with $\text{Zr}(\text{SO}_4)_2$ Aq produces basic sulphates $3\text{ZrO}_2 \cdot 4\text{SO}_3$, 15aq and $6\text{ZrO}_2 \cdot 7\text{SO}_3$, 19aq (P., l.c.).

Zirconates. $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ behaves as a weak acid towards the stronger bases. A few salts have been prepared which are most simply regarded as derived from $\text{Zr}(\text{OH})_2$ by replacing H by alkali and alkaline earth metals; these zirconates are obtained by heating ZrO_2 with bases; they have been examined chiefly by Hiortdahl (A. 137, 34, 236 [1865]).

Sodium zirconates. (1) Na_2ZrO_3 ($= \text{Na}_2\text{O} \cdot \text{ZrO}_2$); obtained by heating ZrO_2 with Na_2CO_3 in the ratio $\text{ZrO}_2 : \text{Na}_2\text{CO}_3$; the crystalline mass thus formed is gradually decomposed by water with separation of amorphous ZrO_2 . (2) Na_2ZrO_4 ($= 2\text{Na}_2\text{O} \cdot \text{ZrO}_2$); obtained by heating ZrO_2 with a considerable excess of Na_2CO_3 to whiteness for a considerable time; decomposed by water, with formation of (3) $\text{Na}_2\text{O} \cdot 8\text{ZrO}_2$, 12aq, which forms hexagonal tablets.

Zirconates of calcium and magnesium were obtained by H (l.c.) by heating to redness mixtures of ZrO_2 with SiO_2 and CaCl_2 or MgCl_2 . Ouvrard (C. R. 112, 1444 [1891]) describes *lithium zirconate*, Li_2ZrO_3 , obtained by fusing ZrO_2 with LiCl and cooling slowly; when Li_2CO_3 was used, and the fused mass was treated with boiling water containing a little acetic acid, pure ZrO_2 remained.

Zirconium, nitride of. In fusing amorphous Zr with Al, in a cracked lime crucible, Mallet (Am. S. [3] 28, 346 [1858]) obtained a dark grey, porous solid, which gave yellowish lustrous microscopic cubes when treated with HClAq ; the crystals were unchanged by *aqua regia* or alkali solutions; when fused with KOH they gave off NH_3 . The yellow crystals were probably a nitride of Zr.

Zirconium, oxides of. Besides zirconia, ZrO_2 , there exists a higher oxide, probably ZrO_3 ; and, possibly, also a lower oxide (?) ZrO .

Zirconium dioxide ZrO_2 (Zirconia. Zirconic anhydride.) Mol. w. not known.

Preparation.—There are many methods for

preparing ZrO_2 from *zirconite*. 1. The mineral is heated to redness and thrown into water, and the least-coloured pieces are finely powdered and levigated; the powder is very strongly heated with four times its weight of Na_2CO_3 in a Pt crucible, and the product is heated with excess of HClAq ; the whole is evaporated to dryness; the residue is digested with water, filtered from SiO_2 , and $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ is ppd. by NH_4Aq . The pp. is washed and dissolved in HClAq , and the solution is nearly saturated with Na_2CO_3 , and boiled with $\text{Na}_2\text{S}_2\text{O}_3$ Aq as long as SO_2 is given off, whereby $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ is ppd. (Berzelius, P. 4, 124; 8, 186; Hermann, J. pr. 31, 77; Chancel, A. 108, 237; Stromeyer, A. 113, 127).—2. Very finely powdered *zirconite* is boiled with conc. HClAq , and the residue is washed with water and dried; 100 g. of the dried powder are added to 400 g. molten NaOH , with which 20 g. NaF have been mixed, and the whole is heated in a nickel crucible until the action ceases, when the molten mass is poured on to a sheet of nickel, and, after solidification, is plunged into water; the portion insoluble in water is dissolved in HClAq , the solution is evaporated to dryness, and treatment with HClAq and evaporation to dryness are repeated several times to remove SiO_2 and HF . The solution in HClAq is then ppd. by NH_4Aq ; the $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ is thoroughly washed by decantation, dissolved in the smallest possible quantity of conc. HClAq , and the solution is evaporated to dryness; the residue is washed in a funnel with conc. HClAq mixed with 4 pts. of alcohol; the washed solid is then repeatedly crystallised from conc. HClAq . The white, lustrous crystals of $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ thus obtained are dissolved in water, and $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ is ppd. by NH_4Aq (Venable, C. N. 64, 315 [1891]; cf. Bailey, Pr. 46, 74 [1889]; cf. Preparation of Zirconium, p. 893). By heating ppd. $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ to c. 560° , ZrO_2 is obtained.

Crystalline zirconia is obtained from the amorphous form (1) by fusing with borax at a very high temperature, and washing with HClAq (Nordenskjöld, P. 114, 612; Knop, A. 157, 363); (2) by fusion with *microcosmic salt* (K., l.c.); (3) by heating to dull redness in dry HCl at a pressure of three atmospheres (Hautefeuille a. Perrey, C. R. 110, 1638); (4) by melting and volatilising in an electric furnace, using a current of 360 amperes and 70 volts (Moissan, C. R. 116, 1232 [1893]); (5) by heating, to dull redness, a salt of Zr with an acid that can be removed by heating, in a current of dry HCl (H. a. P., l.c.).

Properties.—Amorphous zirconia is a white, tasteless, odorous powder; S.G. c. 5.5 insoluble in acids, except in conc. H_2SO_4 (v. Reactions, No. 7) or HFAq . Crystalline zirconia is a transparent, colourless solid; S.G. 5.1 (Moissan, l.c.), 5.42 (Knop, l.c.), 5.7 (Nordenskjöld, l.c.). The crystals are described by N. (l.c.) as quadratic prisms, isomorphous with SnO_2 (tin stone) and TiO_2 (rutile). The crystals are extremely hard; they scratch glass easily (Moissan, l.c.). It is generally said that when ZrO_2 is heated to incipient redness it glows brightly, and becomes denser; but the experiments of Carnelle a. Walker (C. J. 58, 82 [1888]) on the action of heat on $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$

make it probable that the glowing is an accompaniment of the dehydration from approximately $2\text{ZrO}_2 \cdot \text{H}_2\text{O}$ to approximately $24\text{ZrO}_2 \cdot \text{H}_2\text{O}$. Zirconia reacts towards acids as a basic oxide, forming salts ZrX_2 and ZrX_3 (many of which are basic salts); it also decomposes alkali carbonates and some other alkali and alkaline earth salts, when fused therewith, forming zirconates $m\text{ZrO}_2 \cdot n\text{M}_2\text{O}$ (v. *Zirconates*, p. 896).

Reactions.—1. When ZrO_2 is heated to a very high temperature it melts, boils, and volatilises, condensing in crystals; Moissan (*C. R.* 116, 1222 [1893]) effected the volatilisation in a crucible heated in the electric furnace, using a current of 300 amperes and 70 volts. 2. When very strongly heated with excess of carbon, carbides are formed (v. *Carbides*, p. 894). Heating in a carbon crucible in the electric furnace produces Zr (M., l.c.). 3. Heating with magnesium produces Zr , perhaps also an oxide lower than ZrO_2 (Winkler, *B.* 23, 2642; 24, 888; Phipson, *Pr.* 96, 353; Bailey, *Pr.* 46, 74; cf. *Zirconium monoxide*). When heated with magnesium in an atmosphere of hydrogen, spongy ZrH_2 is perhaps produced (v. *Zirconium hydride*, p. 895).—4. ZrCl_4 is formed by heating ZrO_2 mixed with carbon in a stream of chlorine; using bromine produces ZrBr_4 (v. *Bromide and Chloride*, p. 894).—5. ZrF_4 is formed by heating ZrO_2 to dull redness with excess of ammonium fluoride.—6. K_2ZrF_6 is formed by slightly heating ZrO_2 with excess of potassium hydrogen fluoride, boiling with very dilute HFAg , and filtering.—7. $\text{Zr(SO}_4)_2$ is obtained by heating ZrO_2 with excess of a mixture of 2 pts. conc. sulphuric acid and 1 pt. water.

ZIRCONIUM PEROXIDE. By adding $\text{H}_2\text{O}_2\text{Ag}$ and NH_4Ag to a solution of $\text{Zr(SO}_4)_2$, Clève (*B.* [2] 43, 53) obtained an oxide containing more O than ZrO_2 ; to this oxide he gave the formula ZrO_2 . Bailey in 1886 (*C. J.* 49, 149, 481) examined the pp. obtained by adding $\text{H}_2\text{O}_2\text{Ag}$ to solution of $\text{Zr(SO}_4)_2$; according to B., the moist pp. has the composition Zr_2O_5 , and this composition is unchanged after keeping (moist) for some months. In Bailey's paper in 1889 (*Pr.* 46, 74) he gives the composition $\text{Zr}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$ to the oxide ppd. by $\text{H}_2\text{O}_2\text{Ag}$, either from an acid or an alkaline solution of $\text{Zr(SO}_4)_2$, after drying over P_2O_5 ; and the composition Zr_2O_5 after drying at 100° . The oxide $\text{Zr}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ was obtained (*C. J.* 49, 485) by preparing a solution of $\text{Zr(SO}_4)_2$ by heating K_2ZrF_6 with H_2SO_4 , and at once adding $\text{H}_2\text{O}_2\text{Ag}$. Zr peroxide is insol. in very dilute (1 p.c.) $\text{H}_2\text{SO}_4\text{Ag}$ or HClO_4Ag (B., l.c.). Bailey (l.c.) employed the ppn. of $\text{Zr}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$ to separate Zr from Fe, Nb, and Ti.

ZIRCONIUM MONOXIDE (?) ZrO . By heating ZrO_2 and powdered Mg, in the ratio $\text{ZrO}_2:\text{Mg}$, in a stream of H, Winkler (*B.* 23, 2668 [1890]) obtained a black powder, which he allowed to cool in H, then kept for some time in CO_2 , freed from Mg by treatment with dilute HClAg , washed with water containing HCl, then with alcohol, and finally with ether, and dried in *vacuo*. He thus obtained a deep black powder, which was unacted on by HClAg , HNO_3Ag or $\text{H}_2\text{SO}_4\text{Ag}$, even on warming, and which burst to ZrO_2 when heated in air. W. supposed this black powder to be ZrO .

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Zirconium, oxyacid of. Hydrated zirconia, $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$, reacts as a weak acid towards strong bases (v. *Zirconates*, p. 896).

Zirconium, oxybromide of, $\text{ZrOBr}_2 \cdot x\text{H}_2\text{O}$. ZrBr_4 dissolved in water; on evaporation, transparent needle-shaped crystals are formed, to which Mellis (*Z.* [2] 6, 296) gave the composition $\text{ZrOBr}_2 \cdot 7\text{H}_2\text{O}$. By dissolving $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ in HBrAg and evaporating, Weibull (*B.* 20, 1394 [1887]) obtained lustrous needles of $\text{ZrOBr}_2 \cdot 8\text{H}_2\text{O}$, isomorphous with $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$.

Zirconium, oxychlorides of. Various oxychlorides have been described. (1) $\text{ZrOCl}_2 \cdot x\text{H}_2\text{O}$; prepared by dissolving $\text{ZrO}_2 \cdot \text{H}_2\text{O}$ in HClAg and evaporating (for details as to the best conditions v. Weibull, *B.* 20, 1394). Hermann (*J. pr.* 81, 77) gave the formula as $\text{ZrOCl}_2 \cdot 9\text{H}_2\text{O}$; Mellis (*Z.* [2] 6, 296) gave $2\text{ZrOCl}_2 \cdot 9\text{H}_2\text{O}$; and Weibull (l.c.) $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (cf. also Paykull, *B.* 6, 1467; and Bailey, *Pr.* 46, 74). (2) Zr_2OCl_4 ; prepared by Troost a. Hautefeuille (*C. R.* 73, 563) by passing steam and vapour of ZrCl_4 through a red-hot tube. (3) $2\text{Zr}_2\text{O}_2\text{Cl}_4 \cdot 15\text{H}_2\text{O}$; prepared by Endemann (*J. pr.* [3] 31, 219) by adding ether to a warm alcoholic solution of $\text{ZrOCl}_2 \cdot x\text{H}_2\text{O}$.

Zirconium, oxydides of. By adding the calculated weight of BaI_2 in solution, to $\text{Zr(SO}_4)_2$ dissolved in a slight excess of $\text{H}_2\text{SO}_4\text{Ag}$, filtering, evaporating over H_2SO_4 , and removing free I from the residue by CS_2 , Hinshelwood (*A.* 239, 253 [1887]) obtained a white, amorphous powder, easily soluble in water, giving off I in moist air, to which he gave the formula $\text{ZrHO}_2 \cdot \text{H}_2\text{O} \cdot x\text{H}_2\text{O}$ (x probably = 3).

Zirconium, oxysulphide of; v. ZIRCONIUM SULPHIDES (infra).

Zirconium, salts of. The salts formed by the replacement of H of acids by Zr belong to the forms ZrX_2 and ZrX_3 ; many basic salts are known. The following are the chief salts of Zr derived from oxyacids: Arsenates, borates, carbonates, nitrates, oxalates, phosphates, selenites, silicates, sulphates, and sulphites.

Zirconium, silicofluoride of, (?) ZrSiF_6 ; probably obtained by Berzelius by evaporating a solution (?) of $\text{ZrO}_2 \cdot x\text{H}_2\text{O}$ in $\text{H}_2\text{SiF}_6\text{Ag}$ (v. *Lehrbuch*, 3, 505 [5th ed.]).

Zirconium, sulphides of. According to Berzelius (v. *Lehrbuch*, 2, 189 [5th ed.]), a compound of Zr and S is formed by heating the elements together in *vacuo*, or with H. The compound, to which no formula is assigned, is described by B. as a dark-brown coloured powder; unacted on by $\text{H}_2\text{SO}_4\text{Ag}$, HNO_3Ag , or HClAg ; slowly attacked by boiling *aqua regia*; dissolved easily by HFAg , giving off H_2S ; insol. in KOHAg , and decomposed by fusion with KOH to K_2S and ZrO_2 . By strongly heating ZrO_2 in vapour of CS_2 , Fremy (*A. Ch.* [3] 33, 326 [1853]) obtained a graphite-like solid, which was rapidly acted on by HNO_3Ag , with separation of S; Fremy supposed that the substance might be an oxy-sulphide.

Zirconium, sulphocyanide of. By adding Ba(SCN)_2 to $\text{Zr(SO}_4)_2$ solution, Hornberger (*A.* 181, 232 [1876]) obtained a solution, which, he said, contained Zr(SCN)_2 ; this solution quickly decomposed, depositing a yellow solid, while Zr(SCN)_2 remained in solution.

M. M. P. M.
3 M

ADDENDA

[DESCRIPTIVE INORGANIC CHEMISTRY ONLY.]

ALUMINIUM (vol. i. p. 141). *Preparation*.—By electrolysis of a molten mixture of $\text{AlF}_3 \cdot 3\text{NaF}$ with NaCl (Minet, *C. R.* 111, 603 [1890]). The best results are obtained by using the salts in the ratio $\text{AlF}_3 \cdot 3\text{NaF} : 6\text{NaCl}$; details of the quantities to be used, the strength of current, &c., are given by M.

Properties.—Minet (*C. R.* 111, 603 [1890]) gives m.p. of Al as 675° ; and S.G. at 820° as 1.76. The S.H. of Al is given by Richards (*C. N.* 65, 97 [1892]) as 221° at 20° , 232° at 100° , and 2845° at the m.p. = 625° ; the S.H. of molten Al at 650° = 308 , according to Pionchon (*C. R.* 115, 162 [1892]). The molecule of Al in dilute solution in tin is perhaps diatomic (Heycock & Neville, *C. J.* 57, 376 [1890]).

Reactions.—Volatilises in electric furnace, with current of 250 amperes and 70 volts (Moissan, *C. R.* 116, 1429 [1893]). Not appreciably acted on by NO_2 at 500° (Sabatier & Senderens, *C. R.* 115, 236 [1892]). An amalgam is formed by bringing Al into a solution of a mercuric salt (Klandy, *C. C.* 1893 [1] 201; abstract in *C. J.* 61 [11] 376 [1893]). Heated with NaPO_3 in a current of H_2 from 28 to 31 p.c. of the P distils over; P is also obtained by heating Al with any phosphate of Ca or Mg (Rossel & Frank, *B.* 27, 52 [1894]). According to Lunge (*C. N.* 65, 110 [1892]), vessels made of Al may be used for holding articles of food, at least at the ordinary temperature, without danger of the metal being dissolved; this result is confirmed by Klandy (*C. R.* 114, 1536 [1892]).

Aluminium, alloys of (vol. i. p. 143). For an alloy with gold, Al_2Au , v. Heycock & Neville (*C. J.* 65, 74 [1894]).

Aluminium, chloride of (vol. i. p. 144). Nilson & Pettersson (*Z. P. C.* 4, 306 [1889]) made a number of determinations of the V.D. of AlCl_3 ; they find that the compound gradually dissociates above its b.p. until c. 800° , when its V.D. becomes constant and corresponds with the formula AlCl_3 . AlCl_3 may be prepared by heating an alloy of Al and Cu nearly to redness in dry HCl ; AlCl_3 distils over unmixed with any Cu compound (Mabery, *B.* 22, 2658 [1889]). Sabatier (*B.* [3] 1, 88 [1889]) says that crystals of the hydrated chloride after being *in vacuo* for three months at 20° over H_2SO_4 , have the composition $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$.

Aluminium, oxides of (vol. i. p. 146). By heating Al_2O_3 with Mg, in the ratio $\text{Al}_2\text{O}_3 : \text{Mg}$, Winkler (*B.* 23, 780 [1890]) obtained a brownish-black powder which, he says, contained a considerable quantity of an oxide lower than Al_2O_3 , probably AlO . By the incomplete combustion of Al, Pionchon obtained a dark-grey powder, said by P. to have the composition $\text{Al}_2\text{O}_3 = 2\text{AlO} \cdot \text{Al}_2\text{O}_3$ (*C. R.* 117, 828; abstract in *C. J.* 64 [11] 572 [1893]). By heating amorphous Al_2O_3 to in-

ipient redness in HCl gas at a pressure of three atmos., Hautefeuille & Perrey (*C. R.* 110, 1038 [1890]) obtained crystals of corundum. According to Rea (*C. J.* 65, 815 [1894]), Al_2O_3 is unchanged at c. 1750° .

Aluminium, phosphide of (vol. i. p. 146). A grey crystalline powder, Al_2P_3 , was obtained by Rossel & Frank (*B.* 27, 52 [1894]) by heating Al in vapour of P, and then heating the product till P ceased to come off.

AMMONIA (vol. i. p. 196). *Formation*.—According to Loew (*B.* 23, 1443 [1890]), traces of NH_3 are formed by shaking Pt black with very dilute NaOH aq in the air. NH_3 is also formed by the combined action of Pt black and dextrose on KNO_3 aq (L., *loc.*, p. 675).

Properties.—Ludeking & Starr (*Am. S.* [3] 45, 200 [1892]) give S.H. of liquid NH_3 as 8857 . For measurements of the wave-lengths of the lines in the emission spectrum of NH_3 , v. Magnanini (*Z. P. C.* 4, 435 [1889]). Perkin (*C. J.* 65, 689, 728 [1889]) gives M. M. of NH_3 in aqueous and alcoholic solutions; also Mol. W. of various NH_3 salts in solution. Tables showing the solubility of NH_3 in alcohol of various concentrations, at 10° , 20° , and 30° , are given by Delépine (*J. Ph.* [5] 25, 496; v. abstract in *C. J.* 62, 1049 [1892]). For the freezing-points of aqueous solutions of NH_3 , v. Pickering (*C. J.* 63, 151 [1893]).

Reactions.—Dry NH_3 does not combine with dry hydrogen chloride when these gases are mixed (Baker, *C. J.* 65, 611 [1894]). Nor do dry NH_3 and dry carbon dioxide combine (Hughes & Soddy, *C. N.* 69, 138 [1894]). Michel & Grandmougin (*B.* 26, 2565 [1893]) say that the products of passing NH_3 over heated peroxide of Ba, Pb, Mn, or Sr , are N with a little HNO_2 and HNO_3 , and oxide or hydroxide of the metal. The reactions of liquid NH_3 with CrCl_3 and FeCl_3 are described by Christensen (*Zeit. f. anorg. Chemie*, 4, 227; abstract in *C. J.* 64 [11] 469 [1893]).

AMMONIUM COMPOUNDS (vol. i. p. 200).

Ammonium amalgam (vol. i. p. 201). From measurements of the polarisation given by this substance in a solution of NH_4Cl against zinc amalgam, and a comparison of these measurements with the polarisations given by metallic amalgams, Le Blanc concludes that ammonium amalgam really exists (*Z. P. C.* 5, 467; abstract in *C. J.* 58, 2204 [1890]).

Ammonium chloride (vol. i. p. 202). Baker (*C. J.* 65, 611 [1894]) asserts that the V.D. of the dry salt at 350° is 28.7, corresponding with that required by the formula NH_4Cl . B. also says that no reaction occurs when dry NH_4Cl and dry CaO are heated together.

ANTIMONY (vol. i. p. 282). *Reactions*.—Montecatini (*G.* 22, 384, 426) finds that no

appreciable quantity of NH_3 is formed by the interaction of Sb and HNO_3 varying from 2 to 70 p.c. HNO_3 ; NO_2 is practically the only gaseous product of the reaction; when 70 p.c. HNO_3 is used, the residue probably has the composition $(\text{SbO})\text{NO}_2$.

Antimonates (vol. i. p. 285). Several salts have been prepared, by double decomposition from the K salt, by Beilstein and O. v. Biase (C. C. 1889. 803; abstract in C. J. 56, 1123). All the compounds are salts of HSbO_3 ; R. a. J. conclude that the only well-marked antimonates are derived from this acid. Ebel (B. 22, 3044 [1889]) describes several metantimonates.

Antimonites (vol. i. p. 285). For antimonites of K and Na v. Corninbauf (C. R. 115, 1305; abstract in C. J. 61 [11], 171 [1893]).

Antimony, bromide of (vol. i. p. 286). The b.p. of SbBr_3 is given as 275° by Freyer a. V. Meyer (Zeit. f. anorg. Chemie, 2, 1 [1892]).

Antimony, trichloride of (vol. i. p. 286). Boils at 223° (Freyer a. V. Meyer, loc.).

Antimony, pentachloride of (vol. i. p. 287). The V.D. at 218° and 58 mm. pressure was found to be 1417 (corresponding with the formula SbCl_5) by Anschütz a. Evans (A. 253, 95 [1890]). Double compounds of SbCl_5 with HbCl and CsCl are described by Saunders (Am. 14, 152 [1892]), and by Wheeler (Am. S. [3] 46, 269 [1893]).

Antimony, fluoride of (vol. i. p. 287). The double compound $\text{SbF}_3 \cdot 2\text{AmF}$ is described by H. von Helmholtz (Zeit. f. anorg. Chemie, 3, 115 [1893]).

Antimony, hydride of (vol. i. p. 288). The temperature whereat decomposition of SbH_3 begins is given by Braun (B. 22, 3202 [1889]) as c. 150° . For the reactions of SbH_3 with As_2O_3 a. v. Vitali (abstract in C. J. 61 [11], 206 [1893]).

Antimonic oxide (vol. i. p. 290). When heated to dull redness Sb_2O_5 gives off O , forming Sb_2O_3 , which at c. 1750° is further reduced to Sb_2O_3 (Read, C. J. 65, 314 [1891]).

Antimonious sulphide (vol. i. p. 291). Black Sb_2S_3 is formed, according to Mitchell (C. N. 67, 291 [1893]), by passing CO_2 into boiling water with ordinary Sb_2S_3 in suspension. Picton (C. J. 61, 142 [1892]) obtained a colloidal Sb_2S_3 in very fine suspension in water, by allowing solution of tartar emetic to flow into saturated H_2SAq .

Antimony, thio-chlorides and thio-iodides of (vol. i. pp. 292-3). Ouvrard (C. C. 116, 1516 [1889]) describes SbSCl and $\text{Sb}_2\text{S}_2\text{Cl}_2$ obtained by the action of H_2S on SbCl_3 ; and SbSI formed by heating SbI_3 to 150° in dry H_2S , and $\text{Sb}_2\text{S}_2\text{I}_2$ formed by heating Sb_2S_3 with 1 and crystallising from CS_2 .

• **ARSENIC** (vol. i. p. 301). A full account of the different forms of As obtained, along with As_2O_3 , by subliming As in a tube is given by Rutgers (Z. P. C. 4, 403; abstract in C. J. 64 [11], 570 [1893]). Petersen gives the following heats of oxidation, and atomic volumes, of the allotropic forms of As (Z. P. C. 8, 601 [1891]):—

Grey, rhombic	56,830	15.1
Grey-black, amorphous	154,840	15.94
Brown, amorphous	163,503	15.99

Arsenic, bromide of (vol. i. 309). AsBr_3 combines with NH_3 to form $\text{AsBr}_3 \cdot 3\text{NH}_3$ (Besson, C. R. 110, 1258 [1890]).

Arsenates (vol. i. p. 307). For arsenates of Cd v. A. de Schullen (Bl. 13, 1, 473 [1889]); for arsenates of Cu, and of Cu and Na, v. Hirsch (C. C. 1891 [1], 15; abstract in C. J. 60, 644); many double arsenates of K, and of Na, with Cd, Co, Mg, Mn, Ni, and Zn are described by Lefèvre (C. R. 110, 405 [1890]).

For this arsenate of Cu, Hg, Zn; and Zn and Na, v. Preis (A. 257, 173 [1890]).

Arsenites (vol. i. p. 306). For the preparation, by double decomposition from the salt $2\text{KAsO}_4 \cdot \text{As}_2\text{O}_3$, and properties of the arsenites of the following metals v. Biefeld (B. 27, 1019 [1894]):—Al, Ba, Cd, Ca, Cr, Co, Cu, Au, Fe, Pb, Mg, Mn, Ni, Pd, Pt, Ag, Sr, Sn, Ti, U, and Zn (references and criticisms of former investigations are given). Stavenhagen (Zeit. f. anorg. Chemie, 1891, 165) obtained the double salt of K arsenite and sulphate, $\text{KAsO}_3 \cdot 10\text{K}_2\text{SO}_4$, by evaporating solutions of the constituents alternatingly.

Arsenic acid (vol. i. p. 307). For a detailed account of the reaction of H_2S with solutions of HAsO_4 , v. Brauner a. Tomczak (C. J. 53, 145 [1888]).

Arsenious chloride (vol. i. p. 310). According to Besson (C. R. 109, 819 [1890]), AsCl_3 solidifies at -18° , forming white needles; at -30° AsCl_3 absorbs much Cl , forming a liquid which does not solidify at -60° , and which with water gives off much Cl and forms As_2O_3 . Besson (C. R. 110, 1258 [1890]) says that the compound formulated by Rose as $2\text{AsCl}_3 \cdot 7\text{NH}_3$ is really $\text{AsCl}_3 \cdot 4\text{NH}_3$.

• **Arsenious fluoride** (vol. i. p. 310). Moissan (J. Ch. [6] 19, 280 [1891]) prepared AsF_3 by heating As_2O_3 with HF ; he gives b.p. as 63° at 750 mm., and says that it solidifies to white crystals at -85° . Besson (C. R. 110, 1258 [1890]) describes the compound $2\text{AsF}_3 \cdot 5\text{NH}_3$.

Arsenic, trihydride of (vol. i. p. 310). Brun (B. 22, 3202 [1889]) finds that the first products of the action of air, or O , on AsH_3 are solid AsH and H_2O , and the next products are As and H_2O . AsH_3 and H_2S do not react in absence of air at the ordinary temperature, either as gases or in solution (B., loc.). AsH_3 begins to decompose at c. 230° (B., loc.). For the reactions of AsH_3 with AgNO_3 a. v. Vitali (abstract in C. J. 64 [11], 206 [1893]).

• **Arsenious iodide** (vol. i. p. 311). Besson (C. R. 110, 1253 [1890]) describes the compounds $\text{AsI}_3 \cdot 4\text{NH}_3$, and $\text{AsI}_3 \cdot 12\text{NH}_3$.

Arsenious sulphide (vol. i. p. 315). Picton (C. J. 61, 140 [1892]) obtained an aqueous solution of colloidal As_2S_3 , containing also some very finely divided sulphide in suspension, by allowing As_2O_3 to flow into saturated H_2SAq , into which H_2S was continually passing, and removing H_2S by a stream of H .

Arsenic pentasulphide (vol. i. p. 315) As_2S_5 is obtained, according to McCay (Am. 12, 547 [1891]), by passing H_2S for a long time into a hot solution of an alkali dihydrogen arsenate, and then ppg. by a mineral acid.

Arsenic, thiochlorides and thio-iodides of (vol. i. p. 316). Ouvrard (C. R. 116, 1516 [1893]) obtained $\text{As}_2\text{S}_2\text{Cl}_2$ by passing H_2S into

AsCl_3 , and washing the pp. with CS_2 . By heating 1 pt. As_2S_3 with 10 pts. AsCl_3 to 150° he obtained AsSCl .

AZO-IMIDE (v. *Hydrazoic acid*, p. 319, *Addenda*).

BARIUM (vol. i. p. 440). Richards, in 1893, made an elaborate experimental revision of the at. w. of Ba (*P. Am. A.* 28, 1; 29, 55). As a mean result of the most trustworthy experiments, R. adopts 137.1 as the at. w. of Ba ($O=15.96$). Limb (*C. R.* 112, 1434 [1891]) failed to obtain any Ba by electrolysis fused BaCl_2 , or BaCl_2 mixed with NaCl .

Barium, carbide of. By heating a mixture of Ba amalgam and powdered charcoal in H, Maquenne (*C. R.* 114, 361 [1892]) obtained grey BaC_2 , decomposed by water, giving BaO , H_2Aq and C_2H_2 ; v. also Moissan, *C. R.* 118, 683 (abstract in *C. J.* 66 [1], 314 [1894]).

Barium, chloride of (vol. i. p. 441). By bringing BaCl_2 into contact with liquid NH_3 , and allowing the gas to escape at 0° and 760 mm., Joannis obtained $\text{BaCl}_2 \cdot 8\text{NH}_3$ (*C. R.* 112, 337 [1891]).

Barium, fluoride of (vol. i. p. 441). BaF_2 is obtained in microscopic crystals by adding BaCl_2Aq (3-6 p.c.) to boiling KFAg (1 p.c.), boiling, washing, drying, and heating strongly (Moissan, *Bull.* [3], 5, 152 [1891]). Poulenc (*C. R.* 116, 987 [1893]) obtained BaF_2 in well-formed octahedra by fusing amorphous BaF_2 with KHF_4 and KCl .

Barium, nitrides of. Maquenne (*C. R.* 114, 220 [1892]) obtained a mixture, probably containing some Ba_3N_2 , by heating Ba amalgam to redness in a current of N. Berthelot & Matignon (*A. Ch.* (7) 2, 144 [1894]) say that Ba_3N_2 is formed by heating AmN_3Aq with BaO , H_2Aq .

Barium monoxide (vol. i. p. 442). BaO is unchanged at c. 1750° (Read, *C. J.* 65, 313 [1894]); it liquefies at c. $2,000^\circ$, but is not decomposed at c. $2,500^\circ$ (Moissan, *C. R.* 115, 1034 [1892]).

Barium dioxide (vol. i. p. 443). BaO_2 is decomposed by salts of Al, Cr, Co, Fe, &c.; some salts—e.g. those of Ca, Li, K, Na—do not react with BaO_2 (v. Kwasnik, B. 25, 65). For decomposition of BaO_2 by heat v. Le Chatelier (*C. R.* 115, 654; abstract in *C. J.* 64 [1], 71 [1893]).

BERYLLIUM (vol. i. p. 504). Krüss & Morah (*B. 23, 727* [1890]) obtained hexagonal crystals of Be, mixed with BeO, by heating $\text{BeF}_2 \cdot 2\text{KCl}$ to redness with Na. K. a. M. (*l.c.* p. 2552) obtained the value 9.08 for the at. w. of Be by converting BeO into $\text{BeSO}_4 \cdot 4\text{H}_2\text{O}$, and this again to BeO. Gibson (*C. J.* 63, 909 [1893]) describes methods for preparing BeC from *perlyl*.

Beryllium, fluoride of (vol. i. p. 506). Petersen (*Z. F. C.* 5, 263 [1890]) gives the thermal data H_2 . [$\text{BeO} \cdot \text{H}_2\text{O} \cdot 2\text{HFAg}$] = 19.783. The double compound $\text{BeF}_2 \cdot 2\text{AmF}$ is described by H. von Helmholtz (*Zeit. f. anorg. Chemie*, 3, 116 [1893]).

Beryllium, oxide of (vol. i. p. 506). By dissolving BeO, 22g in KOH Aq , Krüss & Morah (*B. 23, 727* [1890]) obtained potassium beryllate $\text{BeO} \cdot \text{K}_2\text{O}$ (?), mixed with K_2CO_3 , as a snow-white, silky solid.

BISMUTH (vol. i. p. 509). The at. w. of Bi was re-determined by Claassen in 1890 (*B. 23, 928* [1890]), by converting Bi into nitrate, and

this into Bi_2O_3 ; the mean result was 209.86 ($O=15.96$). Schneider (*J. pr.* [2] 42, 558; 44, 23 [1891]) criticises Claassen's results and maintains that Marignac's value (almost exactly 208) is as trustworthy as that obtained by C. The molecule of Bi in dilute solution in tin is perhaps diatomic (?) (Heycock & Nevill, *C. J.* 57, 376 [1890]).

Preparation.—Claassen (*l.c.*) says that pure Bi is best prepared by electrolysis a solution of the metal in HNO_3Aq , using a cone of Pt as the negative electrode, then washing with alcohol, and fusing with KCl .

Properties.—Melts at 264° , according to Claassen (*l.c.*): at 269.2° , according to Callendar & Griffiths (*C. N.* 63, 1 [1891]). S.G. 9.7474 (*C.*, *l.c.*; no temperature given!; 9.787 at 0° , 9.673 solid at the m.p., 10.004 liquid at the m.p. (Vicentini, *Rend. Acad. Lincei*, 6 [1], 121, 147 [1891]). For S.G. of liquid Bi from 235° to 280° v. Cattaneo (*Rend. Acad. Lincei*, 7, [1], 88 [1892]). For electrical resistance v. E. v. Aubel (*C. R.* 108, 1102 [1889]).

Reactions.—According to Völey (*Pr.* 48, 458 [1891]), Bi does not dissolve in 30 p.c. HNO_3Aq at 30° if HNO_3 is absent; but Bi dissolves readily in 1 p.c. HNO_3Aq .

Bismuth, bromide of (vol. i. p. 511). BiBr_3 boils at 453° (V. Meyer, *A.* 264, 122 [1891]). Cavazzi & Tivoli (*G. 21* [1], 306 [1892]) describe a lustrous, black, hygroscopic solid, $\text{FBrH}(\text{BiBr}_3)$, obtained by allowing BiBr_3 to fall gradually into PH_3 (abstract in *C. J.* 62, 279).

Bismuth, chloride of (vol. i. p. 512). Boils at 435° – 441° (uncor.) (V. Meyer, *l.c.*). The only double chloride of Bi and K of those hitherto described that exists is $\text{BiCl}_2 \cdot 2\text{KCl}$, 22g, according to Brigham (*Am.* 14, 164 [1892]). B. has also prepared $\text{BiCl}_2 \cdot \text{KCl}$ aq.

Bismuth, fluoride of (vol. i. p. 512). H. von Helmholtz describes the double fluoride $\text{BiF}_2 \cdot \text{AmF}$ (*Zeit. f. anorg. Chemie*, 3, 115 [1893]).

Bismuth, iodide of (vol. i. p. 513). Astre (*C. R.* 110, 525 [1890]) obtained the double iodide $2\text{BiI}_3 \cdot \text{KI}$ by keeping I, KCl , Bi, and water in contact for some weeks, and then crystallising from Et acetate.

Bismuthous oxide (vol. i. p. 513). Claassen (*B. 23, 938* [1890]) gives S.G. as 9.044. Read (*C. J.* 65, 313 [1894]) found Bi_2O_3 to be unchanged at c. 1750° .

Bismuth, oxysulphide of (vol. i. p. 516). By passing dry H_2S into boiling benzene containing Bi_2O_3 in suspension, P. v. Scherpenberg (*C. R.* 1889, [11] 643) obtained $\text{Bi}_2\text{O}_3\text{S}$.

Bismuth, selenide of (vol. i. p. 516). The double compound $\text{Bi}_2\text{Se}_3 \cdot \text{K}_2\text{Se}$ is described by P. v. S. (*l.c.*).

Bismuth, sulphide of (vol. i. p. 516). P. v. S. (*l.c.*) obtained the double compound $\text{Bi}_2\text{S}_3 \cdot \text{K}_2\text{S}$ by fusing Bi_2O_3 with K polysulphide.

BORON (vol. i. p. 524). The at. w. of B has been determined by Abrahall by the analysis of BBr_3 (*C. J.* 61, 650 [1892]); the value obtained was 10.67 ($O=15.96$). Also by Ramsay & Aston (*C. J.* 63, 207 [1893]) by finding the percentage of water in crystalline borax, and by distilling fused borax with HCl Aq , $\text{d CH}_3\text{OH}$ and weighing the residual NaCl ; the values varied about 11, but showed considerable differences.

Himbach (*B.* 26, 164 [1893]), by titrating solutions of borax with standard HClAq, using methyl orange as indicator, obtained the value 10.91 (O = 15.96). The following values for S.H. of amorphous B are given by Moissan & Gautier (*C. R.* 116, 924 [1893]): 0° to 100° = 3066, 0° to 192° = 3407, 0° to 234° = 3573. For atomic refraction of B v. Ghira (*G. Z.* 23 [1], 452; abstract in *C. J.* 64 [11], 517 [1893]).

Preparation.—According to Moissan (*C. R.* 114, 319 [1892]), the methods employed to give amorphous boron yield substances containing from c. 45 to c. 72 p.c. of B. M. (*l.c.* p. 392) says that nearly pure amorphous B is obtained by heating to redness a mixture of one pt. powdered Mg with 3 pts. fused B₂O₃, washing with HClAq, KOH in alcohol, HFaq, and water (the process is tedious, details are given); by fusing this product with 50 pts. B₂O₃, and washing with HClAq &c., a brown powder is obtained containing c. 98.5 p.c. B, with traces of Mg and small quantities of other impurities.

Properties and Reactions.—The properties of amorphous boron are described by Moissan (*C. R.* 114, 617 [1892]). Brown powder; S.G. 2.45. Does not fuse in electric arc, but volatilises (*M.*, *C. R.* 117, 423 [1893]); increases in density when heated to c. 1500° in H₂. Specific electrical resistance = 801 megohms. Burns in air at c. 700°. Combines directly with Br, Cl, (not I), N at c. 1200°, Se, S, (not Te); also with Al, Fe, Mg, Pt, and Ag. Reduces many oxyacids and oxides when heated therewith; HClO₄, HNO₃, HNO₂, and H₂SO₄ are rapidly reduced; As₂O₃ and As₂O₅, CO, N₂O, P₂O₅, SiO₂, steam, and SO₂ are also reduced; many metallic oxides are reduced to metals, often with explosive violence; molten KOH gives off H₂; metallic fluorides are generally decomposed, giving BF₃; many other metallic salts, both in solution and when heated as solids, are reduced by amorphous boron.

Boron, bromide of (vol. i. p. 525). BBr₃ boils at 90° (Freyer & V. Meyer, *Zeit. f. anorg. Chemie*, 2, 1). Ghira (*Z. P. C.* 12, 768 [1893]) gives S.V. 94.72; and S.G. $\frac{d}{4}$ = 2.64985. According to Besson (*C. R.* 112, 1001 [1891]), when a mixture of gaseous HI and BBr₃ is passed through a glass tube at 300°–400° the products are BBr₃, BBr₂I, and BI₃. BBr₃I and BBr₂I are colourless liquids, distilling at c. 125° and 180°; they are rapidly decomposed by air and light. Tarble (*C. R.* 116, 1524 [1893]) says that BBr₃ combines with PBr₃ and PBr₅ to form compounds easily decomposed by water, Cl, or NH₃ in the cold. Besson (*C. R.* 114, 542 [1892]) describes BBr₃·4NH₃, obtained by passing dry NH₃ into BBr₃ in dry CCl₄.

Boron, carbide of, B₂C. Moissan (*C. R.* 118, 556 [1894]) says that B and C combine when amorphous B is mixed with c. 1 its weight of sugar charcoal, and the mixture is heated in the electric furnace for some minutes, using a current of 250–300 amperes and 70 volts. After treating the product with HNO₃Aq, and then with KClO₄ and HNO₃Aq, the carbide remains as a very hard, lustrous, black, crystalline powder; S.G. 2.57; burns very slowly in O at c. 1000°; acted on by Cl below 1000° but not by Br, I, S, P, N, or mineral acids; reacts with molten KOH or KNaCO₃ (abstract in *C. J.* 66 [11], 249 [1894]).

Boron, chloride of (vol. i. p. 525). BCl₃, boiling at 17° (Freyer & V. Meyer, *Zeit. f. anorg. Chemie*, 2, 1). Ghira (*Z. P. C.* 12, 768 [1893]) gives S.G. $\frac{d}{4}$ = 1.48386, and S.V. 81.94.

Boron, fluoride of (vol. i. p. 526). According to Besson (*C. R.* 110, 80 [1890]), BF₃ unites with PH₃ at c. –30° to form 2BF₃·PH₃, decomposed by water giving off H and PH₃.

Ammonium borofluoride is described by Stolba (*C. J.* 1896, [1] 211; abstract in *C. J.* 58, 560).

Boron, hydride of (vol. i. p. 526). Sabatier (*C. R.* 112, 865 [1891]) says that the gas produced by adding HClAq to the brown powder formed by heating B₂O₃ with Mg in H has a very disagreeable odour, burns with a green flame, gives a brown ppt. with AgNO₃Aq, deposits B when passed through a glass tube, at a dull red heat (H coming off), and is decomposed by electric sparks, giving pure H. The gas contains a little B hydride, according to S. (*l.c.*); cf. Winkler (*B.* 23, 772 [1890]).

Boron, iodide of (vol. i. p. 527). BI₃. Prepared by Moissan (*C. R.* 112, 717 [1891]), (1) by heating I and B to 700°–800°; (2) by heating amorphous B (dried in H₂ at 200°), in a stream of dry HI, in a tube of hard glass until the glass nearly softens; (3) by passing HI and BCl₃ vapours through a porcelain tube heated to redness. The product is dissolved in CS₂, shaken with Hg, and allowed to crystallise. Colourless crystals, very hygroscopic, rapidly become coloured in light. Melts at 43° and boils at 210°. Decomposed by water, giving HIAq and H₂BO₃Aq. (For other reactions v. abstract in *C. J.* 60, 979 [1891].) For compounds with NH₃, v. Besson (*C. R.* 114, 542 [1892]; abstract in *C. J.* 62, 771).

Boron, oxide of (vol. i. p. 527). B₂O₃. For reduction by Mg powder, giving Mg boride, v. Winkler (*B.* 23, 772 [1890]). The compound B₂O₃·P₂O₅ (= B₂P₂O₇) is obtained by evaporating H₂BO₃Aq mixed with H₂PO₄, heating to redness, and washing with hot water (G. Meyer, *B.* 22, 2919 [1889]).

Borates (vol. i. p. 529). For some new borates of Li, Rb, and Cs v. Reischle (*Zeit. f. anorg. Chemie*, 4, 166 [1893]). For remarks on the classification of alkali and alkaline earth borates v. Le Chatelier (*C. R.* 113, 1034 [1891]). For a full account of Mn borate, v. Hartley & Ramage (*C. J.* 63, 129 [1893]). The compounds 6FeO·FeBr₃·8B₂O₃ and 6ZnO·ZnBr₂·8B₂O₃ are described by Rousseau & Allaire (*C. R.* 116, 1446; abstract in *C. J.* 64 [11], 518 [1893]).

Boron, phosphide of. According to Besson (*C. R.* 113, 78 [1891]), a phosphide of B is obtained by passing PH₃ into BBr₃, and heating the product, BBr₃·PH₃, to 300°, when it gives HBr and B phosphide. The phosphide is said to be a brown powder, insoluble in water, reacting with boiling conc. alkali solutions to give PH₃; gives off P when heated to redness in N (for other reactions v. abstract in *C. J.* 60, 1418 [1891]).

• **Boron, selenide of**. (B₂Se₃). Obtained, as a yellowish grey powder, decomposed violently by water, giving H₂Se and some Se, by heating B to full redness in a current of H₂Se (Sabatier, *C. R.* 112, 1000 [1891]).

Boron, sulphides of (vol. i. p. 531). For heat of formation of B_2S_3 , v. Sabatier (*C. R.* 112, 862; abstract in *C. J.* 60, 981 [1891]). Moissan (*C. R.* 115, 203 [1892]) gives details of various methods of preparing B_2S_3 , and describes the reactions of this compound (v. abstract in *C. J.* 62, 1393 [1892]). According to M. (l.c. p. 271), boron pentasulphide, B_2S_5 , is obtained by heating BI_3 with rather less than one equiv. of S in CS_2 solution at 60° for many hours. M. describes the compound, which was not obtained pure, as a light white crystalline powder, S.G. 1.85.

BROMHYDRIC ACID (vol. i. p. 532). The V.D. has been determined by Biltz at -15° and -28° (*Z. P. C.* 10, 354 [1892]); the results agree with the V.D. required by the formula HBr. The M. Ms. of HBrAq from 15.47 to 65.59 p.c. HBr have been measured by Perkin (*C. J.* 55, 706 [1889]).

Preparation.—1. By the interaction of P, Br, and H_2O , v. Filoti a. Crosa (*G.* 21, 64 [1891]; cf. Gassman, abstract in *C. J.* 64 [11], 453 [1893]). 2. By passing H_2S into Br covered with water (Recoura, *C. R.* 110, 784 [1890]).—3. By adding H_2SO_4 Aq S.G. 1.41 to KBr (Feit a. Knibierschky, *J. Ph.* [5] 24, 159; abstract in *C. J.* 60, 1320 [1891]; v. also Addyman, *C. J.* 61, 97 [1892]; cf. Léger, abstract in *C. J.* 64 [11], 114 [1893]).

Hydrates.—Pickering (*P. M.* [5] 36, 11 [1894]) has isolated $HE \cdot 3H_2O$ and $HBr \cdot 4H_2O$; the former melting at -48° and the latter at -55.8° .

Reactions.—For the decomposition of HBrAq by H_2SO_4 Aq of different concentrations v. Addyman (*C. J.* 61, 98 [1892]).

BROMINE (vol. i. p. 534). Mol. w. in solution in water or acetic acid = 159.5 (Br.) (Paterno a. Nasini, *B.* 21, 215 [1888]). The V.D.s of Br from 15° to 280° , and at pressures from 75 to 760 mm., have been determined by Perman (*Tr.* 48, 45 [1891]); no indications of dissociation were obtained. For measurements of the absorption of light by Br v. Camichel (*C. R.* 117, 807; abstract in *C. J.* 64 [11], 561 [1893]).

Bromates (vol. i. p. 538). **Lithium bromate** $LiBrO_3$, prepared by the interaction of $Ba(BrO_3)_2$ Aq and Li_2SO_4 Aq (Potilitzin, *J. R.* 22, 392; abstract in *C. J.* 62, 1275 [1892]). **Potassium bromate** $KBrO_3$. The decomposition of this salt by heat has been studied by Cook (*C. J.* 65, 802 [1894]); decrepitation occurs at c. 180° , with evolution of Br; the salt fuses at a higher temperature, and O is evolved, without any Br, until KBr remains; no oxy-compounds are formed.

Strontium bromate, being, as to decompose at c. 240° ; the principal change is to $SrBr_2$ and O , but SrO is also formed (Potilitzin, *J. R.* 22, 454; abstract, with summary of quantitative results, in *C. J.* 64 [11], 11 [1893]).

CADMIUM (vol. i. p. 354). Determinations of heat v. have been made by Partridge (*Am. S.* [3] 40, 377 [1891]), and by Morse a. Jones (*Am. J.* 14, 261 [1892]). P. converted $CdCO_3$ into CdO by heating, $CdSO_4$ into CdS by heating in H_2S , and $CdCl_2$ into CdS by heating in H_2S . M. a. J. converted Cd into $Cd(NO_3)_2$, and this into CdO by heating. The results all lie about 112 (*v. abstract in C. J.* 60, 399; cf. Clarke, *ibid.* 390 [1891], and 62, 1397 [1892]). Lorimer a. Smith

(*Zeit. f. anorg. Chemie* [1, 364 [1892]) obtained values varying from 112.182 to 111.908 ($O=16$). The molecule of Cd in dilute solution in tin may be diatomic (v. Heycock a. Neville, *C. J.* 57, 376 [1890]). Cd melts at 320.68° , according to Callendar a. Griffiths (determined by Pt thermometer, *C. N.* 63, 1 [1891]). For the life-spectrum of Cd v. Ames (*P. M.* [5] 30, 33 [1890]). According to Williams (*Ann.* 14, 273 [1892]), Cd crystallises in hexagonal and polyhedral forms; axial ratio $a:c=1:1.6554$. Cd is superficially oxidised at a dull-red heat by nitric oxide (Sabatier a. Senderens, *Cr. R.* 114, 1429 [1892]). Montemartini (*G.* 22 [1] 250; v. abstract in *C. J.* 62, 1278 [1892]) has analysed the gases produced by the interaction of Cd and nitric acid, with excess of HNO_3 Aq (27.5 p.c.) at 8° , N , N_2O , N_2O and NH_3 are produced.

Cadmium, alloys of (vol. i. p. 655). For an alloy with gold, $CdAu$, v. Heycock a. Neville (*C. J.* 61, 914 [1892]; cf. *ibid.* 65, 65 [1894]). For alloys with copper, gold, and silver, prepared by immersing Cd in solutions of salts of the other metals, v. Mylius a. Fromm (*B.* 27, 630 [1894]).

Cadmium, bromide of (vol. i. p. 655). For the double compounds $CdBr_x \cdot xCsBr$, $x=1, 2$, and 3, v. Wells a. Walden (*Zeit. f. anorg. Chemie*, 5, 266 [1893]).

Cadmium, chloride of (vol. i. p. 655). Kwasnik (*Ar. Ph.* 229, 569; abstract in *C. J.* 62, 566 [1892]) describes $CdCl_2 \cdot 2NH_3$ and $CdCl_2 \cdot NH_3$. For the double compounds $CdCl_2 \cdot CsCl$ and $CdCl_2 \cdot 2CsCl$, v. Wells a. Walden (l.c.). Double compounds with HCl , NH_4Cl , $LiCl$, and KCl , of the form $CdCl_2 \cdot MCl$, aq., are described by Clusseau (*A. Ch.* [6] 30, 5; v. abstract in *C. J.* 66 [11], 18 [1894]).

Cadmium, fluoride of (vol. i. p. 655). CdF_2 is obtained by (1) the interaction of HF and Cd at a red heat; (2) the interaction of HF and fused $CdCl_2$, or CdO at a red heat; it is a colourless, transparent solid; S.G. 6.64; somewhat soluble water, insoluble alcohol of 95° (Poulenc, *C. R.* 116, 591 [1893]).

Cadmium, iodide of (vol. i. p. 656). For the double compounds $CdI_x \cdot xCsI$, when $x=1, 2$, and 3, v. Wells a. Walden (l.c.).

Cadmium, oxides of (vol. i. p. 656). CdO is unchanged at c. 1750° (Wald, *C. J.* 65, 313 [1894]).

According to Kouriloff (*J. R.* 22, 171; abstract in *C. J.* 62, 1278 [1892]), the compound $CdO_2 \cdot CdO \cdot H_2O$ is obtained by heating $CdO \cdot H_2O$ with H_2O Aq. Moré a. Jones (*Am. J.* 12, 488; abstract in *C. J.* 58, 1376 [1890]) obtained small crystals, which they say were cadmium oxide Cd_2O_3 , by gently heating $CdOH$; the hydroxide was obtained by heating $CdCl_2$, $CdBr_2$, or CdI_2 with excess of Cd, to the melting-point, in N , or *vacuo*, and heating with water, when $CdCl_2$, $CdBr_2$, or CdI_2 dissolved, a little $CdO \cdot H_2O$ separated, and $CdOH$ remained as a white amorphous powder.

Cadmium, salts of (vol. i. p. 656). For the electrical conductivities of very dilute solutions of $CdBr_2$, $CdCl_2$, CdI_2 , K_2CdF_6 , $Cd(NO_3)_2$, and $CdSO_4$, v. Wershoven (*Z. P. C.* 5, 481 [1890]).

Cadmium, sulphide of (vol. i. p. 657). Two forms (and perhaps more) of CdS seem to exist, one lemon-yellow and the other red; they differ

ingly in S.G., and in crystalline form; the yellow is said to change to the red by friction (v. Buehner, *Chem. Zeit.* 11, 1087, 1107; 15, 778; von Klobukoff, *J. pr.* [2] 39, 412; *abstracts* in *C. J.* 54, 234 [1888]; 56, 946 [1889]; 62, 778 [1892]). A solution of colloidal C.S. was obtained by Prost (*Ca C.* 1888, 32; *abstract* in *C. J.* 54, 653 [1888]) by completely ppg. an ammoniacal solution of CdSO_4 by H_2S , washing well, suspending the pp. in water and passing in H_2S . A solution with 4 grms. CdS per litre remained clear for many days; one with 11 grms. coagulated in 2½ hours.

CAESIUM (vol. i. p. 657). According to Beketoff (*n. abstract* in *C. J.* 62, 274 [1892]), Cs is obtained by heating CsOH with c. 4 its weight of Al.

Cesium, haloid compounds of (vol. i. p. 658). A series of compounds of the form CsX , where $\text{X} = \text{Br}$, I , or Br and I , Cl , Br and I , &c., is described by Wells & Penfield (*Am. S.* [3] 43, 17; *abstract* in *C. J.* 62, 773 [1892]). Double compounds of Cs haloids with haloid compounds of Cd, Cu, Mg, Hg, Pb, and Zn are described by Wells (and others) (*Am. S.* [3] 41, 221; *Zeit. f. anorg. Chemie*, 3, 195; 5, 266, 273, 300, 304, 306; *abstracts* in *C. J.* 64 [11], 67, 322 [1893]; 66 [11], 45, 47 [1894]).

Cesium, hydroxide of (vol. i. p. 658). S.G. d_{40}^{20} 4.0178; $[\text{CsOH}, \text{Al}] = 15, 876$; $[\text{CsOH}, \text{HCl}, \text{Al}] = 13, 790$ (Beketoff, *C. C.* 1891, [11] 451).

Cesium, oxide of (vol. i. p. 658). According to Beketoff (*J. R.* 25, 433; *abstract* in *C. J.* 60 [11], 234 [1891]), Cs_2O reacts with slightly moist H to give Cs and CsOH .

CALCIUM (vol. i. p. 663). The molecule in dilute solution in tin may be diatomic (v. Heycock & Neville, *C. J.* 57, 376 [1890]).

Calcium, carbide of. By heating 120 g. CaCO_3 with 70 g. sugar charcoal in the electric furnace with a current of 350 amperes and 70 volts, Moissan (*C. R.* 118, 501 [1894]) obtained lustrous, yellow crystals of CaC_2 ; S.G. 2.22 at 18° ; insoluble in most solvents; reacts with Cl , Br , and I at 250° – 350° ; burnt to CaCO_3 by O at a red heat; interacts violently with water, giving off pure acetylene, and with steam giving CaCO_3 , C_2H_2 , and C_2H_4 (*abstract* in *C. J.* 66 [1], 313 [1894]).

Calcium, oxide of (vol. i. p. 666). CaO is unchanged at c. 1750° (Read, *C. J.* 65, 313 [1894]). According to Veley (*C. J.* 63, 821 [1893]; 66, 1 [1894]), dry CaO does not appreciably combine with dry CO_2 , SO_2 , or Cl_2 below 300° . Baker (*C. J.* 65, 611 [1894]) says that dry CaO does not react with dry SO_2 , nor with dry NH_4Cl . Moissan (*C. R.* 115, 1084 [1892]) obtained crystals of CaO by heating ordinary lime in the electric furnace.

Calcium, oxychloride of (vol. i. p. 666). Prepared by boiling CaO with conc. CaCl_2 ; crystallises in thin, lustrous needles; decomposed by water, alcohol, &c.; dissolves in glycerin. Composition is probably $3\text{CaO} \cdot \text{CaCl}_2 \cdot 15\text{aq}$ (Zachorsky, *Zeit. f. anorg. Chemie*, 3, 84 [1893]).

Calcium, oxyiodide of. By heating CaO with CaI_2 in a sealed tube at 150° for 6 hours, Tassilly (*BL* [8] 9, 629 [1893]) obtained needles of $\text{CaI}_2 \cdot 3\text{CaO} \cdot 18\text{aq}$.

CARBON (vol. i. p. 684).

Diamond. Moissan (*C. R.* 116, 218; 118, 320; *abstracts* in *C. J.* 64 [11], 275; 66 [11], 184 [1893 and 1894]) obtained grey-black carbonado by dissolving C in iron, heating to 2000° – 3000° , and rapidly cooling the exterior by water or by plunging into a bath of melted lead; the liquid interior expands as it cools and produces a very high pressure. Diamond blackens, swells, and changes to graphite in the electric furnace (*M. C. R.* 117, 423 [1893]). For various reactions of diamond, v. Moissan (*C. R.* 116, 460; *abstract* in *C. J.* 64 [11], 319 [1893]).

Graphite. For accounts of graphites prepared in different ways, the compositions of the graphitic oxides obtained, and the H.F.s of these oxides, v. Berthelot & Petit (*C. R.* 110, 101, 106; *abstract* in *C. J.* 64, 448 [1890]). For the action of conc. HNO_3 on various graphites, v. Luzi (*B.* 24, 4085; 26, 1412 [1892 and 1893]).

Amorphous carbon. Mixer (*Am. S.* [3] 45, 363; *abstract* in *C. J.* 61 [11], 671 [1893]) describes the interactions of charcoal and N, S, O, and the halogens. According to Ernst (*J. pr.* [2] 48, 31; *abstract* in *C. J.* 64 [11], 461 [1893]), the composition of the products of combustion of coke (CO and CO_2) depends almost wholly on the temperature; the maximum formation of CO is at c. 700° , at $1,000^\circ$ CO is the only product.

Allotropy of carbon. The following heats of combustion, and atomic volumes, are given by Petersen (*Z. P. C.* 8, 601 [1891]):—

	(C.O.)	At. volume.
Amorphous . . .	96,530 to 96,980	6.7 to 8
Graphite . . .	93,360	5.8
Diamond . . .	93,240 to 94,550	3.4

For the reactions of various forms of C with $\text{K}_2\text{Cr}_2\text{O}_7$ and H_2SO_4 , v. Wiesner (*M.* 13, 871; *abstract* in *C. J.* 62, 1273 [1892]); and with HNO_3 and KClO_4 , v. Schutzenberger (*C. R.* 111, 774; *abstract* in *C. J.* 60, 265 [1891]).

Carbon, tetrabromide of (vol. i. p. 688). Collie (*C. J.* 65, 262 [1891]) finds that very many compounds of carbon give CBr_4 when heated with NaOH and Br .

Carbon, bromochlorides of (vol. i. p. 688). The three compounds CBrCl_3 , CBr_2Cl_2 , and CCl_3Br are formed by heating CHCl_3 and Br to 225° in a sealed tube (Besson, *C. R.* 114, 222 [1892]).

Carbon, tetrafluoride of, CF_4 . Mol. w. 88.87. V.D. 44.6. Prepared by the direct union of C (purified lampblack) and F at the ordinary temperature; by the reaction of F with CCl_4 , slightly heated, or with CHCl_3 at 100° , or with CHI_3 (Moissan, *C. R.* 110, 296, 951; *abstracts* in *C. J.* 58, 557, 944 [1890]); also by heating AgF with CCl_4 to 220° in a sealed tube (Chabrie, *C. R.* 110, 279 [1890]). M. recommends to pass vapour of CCl_4 over AgF at 195° – 200° , to let the vapours pass through a serpentine tube kept at -23° , and to collect the gas over Hg ; the gas is kept in contact with fragments of caoutchouc (to remove CCl_4), then shaken with absolute alcohol, in which it dissolves, and then expelled by heat, collected and shaken with H_2SO_4 (to remove alcohol vapour); metal vessels must be used. CF_4 is a colourless gas, liquefying at -125° and 760 mm. pressure, or at 20° under

a pressure of 4 atmos. Other fluorides seem to be formed along with CF_4 ; Chabré (L.c.) says that AgF and C_2F_4 yield C_2F_6 .

Carbon; tetra-iodide of (vol. i. p. 689). Moissan (C. R. 113, 19; abstract in C. J. 60, 1420 [1891]) prepares CI_4 by heating CCl_4 (free from CHCl_3) with excess of HI to 90° in a sealed tube, washing the crystals with NaHSO_3 aq, drying, and slowly subliming *in vacuo*. CI_4 reacts with Cl_2 to form CCl_4 and chlorides of I ; reduced to CHI_3 by H at 140° (for other reactions v. M., L.c.).

Carbon monoxide (vol. i. p. 689). For some experiments on the sparking of CO , with the formation of brown solids, v. Berthelot (C. R. 110, 609) and Schutzenberger (C. R. 110, 560; abstracts in C. J. 58, 691 [1890]). Winkler (B. 24, 878 [1891]) finds that CO is reduced to C , at a full red heat, by Mg ; carbides of Mg are probably formed (cf. W., B. 23, 2612 [1890]).

Carbon dioxide (vol. i. p. 691). For S.H. of CO_2 , v. Kurnakoff (J. R. 22, 493; abstract in C. J. 64 [11], 5 [1893]). CO_2 is reduced by heating to redness with Mg , amorphous C , and some CO being formed (Winkler, B. 23, 2642; 24, 878 [1890-91]). Dry CO_2 is said not to combine with dry NH_3 (Hughes & Soddy, C. N. 69, 188).

Carbon, oxychloride of (vol. i. p. 692). COCl_2 becomes viscid, but remains clear, at -75° (Haase, B. 26, 1052 [1893]).

Carbon disulphide (vol. i. p. 693). The contractions observed when mixtures of CS_2 and air are exploded show that the reaction is more complicated than is shown by the equation $\text{CS}_2 + 3\text{O}_2 = \text{CO}_2 + 2\text{SO}_2$; the volume of CO_2 formed is, practically, in accordance with the equation, but the volume of SO_2 is smaller; some of the N of the air is oxidised (v. Podler, C. J. 57, 625 [1890]). By heating CS_2 with excess of *aqua regia*, Schlagdenhauffen & Bloch (J. Ph. [5] 28, 241 [1893]) obtained $\text{SO}(\text{OCCl}_2)\text{Cl}$. Decomposition of CS_2 , heated in dry N , begins at 216° , and explosion with O at a higher temperature (Baker, C. J. 65, 611 [1894]).

Tricarbon disulphide C_3S_2 . B. von Lengyel (Z. 26, 2960 [1893]) obtained this compound by keeping the vapours of CS_2 in an electric arc between C poles for some hours, filtering off the black substance formed, allowing the red filtrate to stand over Cu for 6 to 8 days, and evaporating in a current of dry air. C_3S_2 is a deep-red liquid, B.G. 1.27389; the vapour, even in minute quantities, causes violent catarrh; can be distilled, with partial change to a black solid, at 60° - 70° and reduced pressure; insoluble in water, but dissolved by EtOH , Et_2O , CS_2 , CHCl_3 , or C_2H_6 . A conc. solution in CS_2 deposits a black solid; the same solid is formed by gently heating the liquid, if heating to 100° - 120° is rapid the change is explosive. The black solid is probably a polymeride. A solution of C_3S_2 in CS_2 reacts with Br to form $\text{C}_3\text{S}_2\text{Br}_2$. (For other reactions, v. abstract in C. J. 66 [11], 91 [1894].)

Carbon, thiobromide of, $\text{C}_3\text{S}_2\text{Br}_2$; formed by the action of Br on a solution of C_3S_2 in CS_2 (v. supra).

Carbon, thiochloride of (vol. i. p. 695). The polymeride of thio-carbonyl chloride has the molecular formula $(\text{OSCl})_n$, according to the

cryoscopic determinations of Carrara (v. 20 [12]; abstract in C. J. 66 [11], 15 [1894]).

CEBIUM (vol. i. p. 723). For details regarding the preparation of Ce compounds free from compounds of Di and La , v. Schottländer (B. 28, 378 [1892]); also Bricout (C. R. 118, 146 [1894]).

Cerium, hydride of. According to Winkler (B. 24, 873 [1891]), a compound of Ce and H , probably CeH_3 , is formed by reducing CeO_2 by Mg in presence of H .

Cerium dioxide (vol. i. p. 725). CeO_2 is unchanged at c. 1750° (Kead, C. J. 65, 813 [1894]).

CHLORHYDRIC ACID (vol. ii. p. 5). Biltz (Z. P. C. 10, 854 [1892]) finds that the V.D. at -77° agrees with the formula HCl . Perkin (C. J. 55, 793, 705 [1889]) has determined M. M. of HCl aq and HCl in iso-amyl oxide; the values obtained for HCl in aq are c. double those for HCl in iso-amyl oxide. For measurements of the E.C. of HCl in different solvents, v. Kablukoff (Z. P. C. 4, 429 [1889]). For revised tables giving S.G. of HCl aq, v. Lunge & Marchlewski (Zeit. f. anorg. Chemie, 1891, 135).

For the relations between the number of molecules of HCl required to ppt. one mol of different chlorides, and the reduction of the freezing-points of solutions of the chlorides and of HCl , v. Engel (C. R. 117, 845; abstract in C. J. 66, 40 [1894]).

Bailey & Fowler (C. J. 53, 755 [1888]) find that when HCl stands over P_2O_5 , the gas is absorbed, with production of POCl_3 and HPO_3 ; and that when HCl and O stand over Hg an oxychloride, probably $\text{Hg}_2\text{OCl}_2\text{H}_2\text{O}$, is formed. Bixler (C. J. 65, 611 [1891]) states that dry HCl does not combine with dry NH_3 when the gases are mixed.

CHLORINE (vol. ii. p. 10). For the S.G. of liquid chlorine from -80° to 77° , and the vapour pressures from -88° to 146° , v. Knietsch (A. 259, 100 [1890]). For the preparation of Cl for use in the laboratory, v. Klason (B. 23, 330; abstract in C. J. 53, 415 [1890]). Shenstone (C. J. 61, 445 [1892]) finds that Cl obtained by heating PtCl_4 always contains some HCl and O , with water, and perhaps a trace of N . Cl expands when brought into sunlight. Richardson (P. M. [5] 82, 277 [1891]) has constructed an instrument wherein the expansion is used to measure the intensity of light. Baker (C. J. 65, 611 [1894]) found that no explosion occurred when a mixture of equal vols. of dry Cl and dry H was exposed to bright sunlight; and that after exposure to bright sunshine for two days, and to diffused light for two days, more than a quarter of the mixture remained unchanged.

Podler (C. J. 57, 618 [1890]) has examined the interaction of Cl and water in tropical sunlight; he finds that there is very little action, unless there is an extremely large excess of water. With very much water and little Cl , exposed to the full light of the sun in the hot season in India, the main reaction is $2\text{H}_2\text{O} + 2\text{Cl}_2 + \text{Aq} = 4\text{HCl}$ aq + O_2 ; with diffused sunlight HCl aq and HClO aq are formed at first, and finally HCl aq, HClO aq, and O_2 . Harker (Z. P. C. 9, 678 [1892]), from an extended investigation of the explosion of mixtures of Cl , H , and O , concluded that when there is insufficient H to

decomposition of the H between the Cl and O occurs; and that the product of the numbers of molecules of HCl and O, divided by the product of the numbers of molecules of H₂O and Cl, is a constant, or, in other words, that the law of Guldberg and Waage holds good. According to Gautier and Chappy (C. R. 113, 597 [1891]), there is no reaction between Mg or Zn and liquid Cl at the ordinary temperature, very little reaction with Fe or Ag, and rather more with Cu.

Chlorates (vol. i., p. 18). Spring and Prost (Bl. [3] 1, 340 [1893]) have determined the quantities of Cl obtained by decomposing by heat chlorates of Al, Ba, Cu, Pb, Hg, K, Ag, Na, and Zn; the amount of Cl varied from .02 p.c. from KClO₃ to 14.45 p.c. from Zn(ClO₃)₂.

Calcium chlorate. Dry Ca(ClO₃)₂ melts between 300°-350°, having previously given off from 8 to 5 p.c. of its weight of O; the rate of evolution of O increases, at 330°, until c. 60 p.c. of the total O is given off, after which the rate decreases. For the quantities of O evolved, of Ca(ClO₃)₂ decomposed, and of CaCl₂ and Ca(ClO₂)₂ formed, v. abstract in C. J. 62, 1275 [1892].

Potassium chlorate. McLeod (C. J. 55, 184 [1890]) concluded from his experiments that when KClO₃ is heated with MnO₂ some KMnO₄ is formed and again decomposed (v. MANGANESE PEROXIDE, vol. iii. p. 183), and that Cl is always given off in this reaction. In 1893 (B. 26, 1790) Brunck stated that Cl is not given off when KClO₃ and MnO₂ are heated together, but that ozone is produced. McLeod (C. J. 65, 202 [1894]) has proved that Cl is produced in the reaction. Fowler and Grant (C. J. 57, 272 [1890]) have studied the influence of various oxides on the decomposition of KClO₃ (references are given to older memoirs); they support McLeod's view of the reaction with MnO₂, and think that the oxides of Fe, Co, Cu, and Ni react similarly to MnO₂; acidic oxides, such as V₂O₅, U₃O₈, and WO₃, cause evolution of O accompanied by much Cl, a vanadate, uranate, or tungstate being also formed; powdered glass or sand also assists the reaction, but only when very finely divided (v. summary of conclusions, C. J. 57, 281-2). According to Thozon and Perry (C. J. 61, 925 [1892]), the main reaction which occurs when an intimate mixture of KClO₃ and iodine is heated is 2KClO₃ + I₂ = 2KIO₃ + Cl₂, and some of the Cl reacts with unchanged I to form ICl and ICl₃. Basset (C. J. 57, 760 [1890]) examined the reactions between KClO₃, water, and iodine; he concluded that the main reaction, at 60°, in the presence of a very small quantity of HNO₃, is as shown by the equation 6I₂ + 10KClO₃ + 6H₂O + Aq = 6KHIO₃ + 4KClAq + 6HClAq; in evaporating the solution to dryness, Cl was given off, and the results of several experiments led to the representation of the change produced by evaporation to dryness as 12KHIO₃ + 8KCl + 12HCl = 11KHIO₃ + 9KCl + 6H₂O + ICl + ICl₂HCl + 4Cl₂. For determinations of the quantities of oxidising gases (Cl and oxides of Cl) removed by passing air through KClO₃Aq mixed with HClAq, v. Pendlebury and McKillop (C. S. Proc. 1893-4, [No. 123] 211).

Strontium chlorate. For experiments on the

decomposition of this salt by heat, giving SrCl₂, Sr(ClO₂)₂, and O, v. Potilitzin (J. R. 21, 451; abstract in C. J. 58, 698 [1890]).

CHROMIUM (vol. ii. p. 162). S.H. of pure Cr (3° to 99°) = 12162 (Jäger and Kriss, B. 22, 2028 [1889]). The at. w. of Cr was re-determined by Rawson in 1889 (C. J. 55, 219), by strongly heating (NH₄)₂Cr₂O₇, measuring the N given off, and weighing the Cr₂O₃ that remained; also by reducing (NH₄)₂Cr₂O₇Aq to CrCl₃Aq by HClAq and alcohol, pp. by NH₄Aq, and weighing Cr₂O₃ produced; the mean value thus obtained was 52.06, or 51.98 reduced to 0° and a vacuum (O = 15.96). Menckie in 1891 (A. 261, 339; abstract in C. J. 60, 882 [1891]) re-determined the at. w. of Cr by estimating (1) Ag and Cr, and also O, in Ag₂Cr₂O₇ and in Ag₂CrO₄.NH₃, (2) O in K₂Cr₂O₇; (3) Cr in (NH₄)₂Cr₂O₇; the extreme values, from thirty-six experiments, were 52.12 and 51.83; twenty-eight of the experiments gave values between 51.9 and 52. According to Prinz (C. R. 116, 392 [1893]), Cr crystallises in minute cubes with pyramidal faces. For the absorption spectra of salts of Cr, v. Lapraik (J. pr. [2] 47, 308 [1893]).

Preparation.—Glatzel (B. 23, 3127 [1890]) says that almost perfectly pure Cr can be obtained by reducing CrCl₃.KCl by Mg powder (for details v. abstract in C. J. 60, 152 [1891]). Placet (C. R. 115, 945 [1892]) prepares Cr by electrolysis a solution of Cr alum, containing an alkali sulphate and H₂SO₄. Moissan (C. R. 116, 349 [1893]) says that Cr can be obtained by reducing a mixture of Cr₂O₃ and C in the electric furnace, using a current of 50 volts and 100 amperes, and then breaking up the product, which contains from 8.6 to 12.9 p.c. C, and heating it, mixed with more Cr₂O₃, again in the electric furnace in a carbon crucible.

Chromic acid (vol. ii. p. 154). Miss Field (C. J. 61, 405 [1892]) has found that only Cr₂O₃ is obtained by working according to Moissan's directions for preparing H₂CrO₄. Determinations of the increase in the b.p. of water caused by solution of Cr₂O₃ led to the conclusion that an aqueous solution of Cr₂O₃ contains some H₂CrO₄, and probably also H₂CrO₃.

Chromic bromide CrBr₃ (vol. ii. p. 161). Recoura (C. R. 110, 1029, 1193) obtained green CrBr₃.6H₂O by boiling saturated CrO₃Aq with a large excess of HBrAq and concentrating; deliquescent crystals, soluble alcohol, insoluble ether. Unchanged when kept solid, but solution soon becomes blue and then violet, with rise of temperature. By boiling a green solution, then saturating with HBr while cold, filtering, and drying the pp. thus formed on porous plates, crystals of the blue variety, CrBr₃.6H₂O, were obtained; very soluble water, insol. alcohol. Heat of solution of blue crystals = 28,700; and of green = 13,600. The blue solid changed to the green at 100°. (For more details v. abstract in C. J. 58, 1068 [1890]).

Chromic chloride CrCl₃ (vol. ii. p. 161). Marchetti (G. 22 [11], 375 [1892]) finds that the molecular lowering of the freezing-point of water by the violet form of CrCl₃ is considerably greater than that caused by the green form.

Chromic fluoride, CrF₃ (vol. ii. p. 162) Fabrig (G. 20, 582 [1890]) obtained CrF₃.9H₂O as a green crystalline pp., by adding excess c

NH_4FAq gradually to a cold solution of violet $\text{Cr}_2(\text{SO}_4)_3$. Slightly sol. water; insoluble NH_4FAq or alcohol; heating in air leaves Cr_2O_3 . Poulenc (*C. R.* 116, 253 [1893]) obtained CrF_3 in green crystals by heating CrCl_3 , Cr_2O_3 , or $\text{CrF}_3 \cdot x\text{H}_2\text{O}$ in HF.

Chromous fluoride. According to Poulenc (*l.c.*), CrF_2 is formed by heating Cr to redness in HF, or by the interaction of CrCl_3 and HF at the ordinary temperature. CrF_2 , after fusion, is described as a transparent, green, crystalline mass; S.G. 4.11; slightly sol. water, insol. alcohol. Heated in air it gives Cr_2O_3 . (For more details *v. abstract in C. J.* 64 [11], 281 [1893].)

Chromic oxide Cr_2O_3 (vol. ii. p. 464). Moissan (*C. R.* 115, 1034 [1892]) found that Cr_2O_3 melted to a black mass, dotted with black crystals, in an electric furnace, using a current of 55 volts and 30 ampères.

Chromium trioxide CrO_3 (vol. ii. p. 164). For action of water *v. CHROMIC ACID*, p. 905. Reduced to Cr_2O_3 by NO at the ordinary temperature (Senderens *a. Sabatier, C. R.* 114, 1476 [1892]). For the reaction of CrO_3 with Q and $\text{BaO} \cdot \text{H}_2\text{Aq}$ —said to give a ppt. approximately BaCrO_4 —*v. Pèchard, C. R.* 113, 39 (*abstract in C. J.* 60, 1431 [1891]).

Chromium salts (vol. ii. p. 167). According to Recoura (*C. R.* 112, 1439; *abstract in C. J.* 60, 1430 [1891]), the green solutions obtained by heating solutions of the normal violet chromic salts contain free acid and a soluble basic salt; in the case of the sulphate this soluble basic salt is said to be $2\text{Cr}_2\text{O}_3 \cdot 5\text{SO}_4$. For preparation of green soluble normal sulphates *v. Recoura, C. R.* 112, 857 (*abstract in C. J.* 62, 411 [1892]).

CHROM-AMMONIUM COMPOUNDS (vol. ii. p. 158). Petersen (*Z. P. C.* 10, 580 [1892]) finds, by cryoscopic determinations, that the formulae usually assigned to the chief salts of this class are probably molecular. For a discussion of the constitution of these salts *v. Jørgensen (J. pr.* [2] 42, 206; 45, 274).

CHROMATES; and derivatives (vol. iii. p. 154).

Ammonium chromates. According to Jäger *a. Krüss (B.* 22, 2028 [1889]), normal ammonium chromate has not hitherto been obtained pure; they prepare the pure salt by adding excess of NH_3 Aq. S.G. 9 to CrO_3 Aq. free from H_2SO_4 Aq., warming until the solid that separates dissolves, and placing in a freezing mixture. $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ crystallizes in long, monosymmetric, golden needles, *a:b:c* = 1.9603:1.24452; S.G. 1.886 at 11°.

Ammonium trichromate $(\text{NH}_4)_3\text{Cr}_2\text{O}_7$ is prepared by J. a. K. (*l.c.*) by dissolving $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ in hot conc. CrO_3 Aq. concentrated, and drying at 100° the fed crystals that separate on cooling; S.G. 2.342 at 18°; explodes at 190°, giving off NO , and leaving Cr_2O_3 .

Ammonium tetrachromate $(\text{NH}_4)_4\text{Cr}_2\text{O}_7$ is formed by dissolving the trichromate in warm HNO_3 Aq. S.G. 1.09, and letting cool slowly; S.G. 2.343 at 10°; melts at 170°, and suddenly decomposes at 175°, giving off NO and leaving Cr_2O_3 . J. a. K. (*l.c.*) failed to obtain hexachromate; they say that no nitro-chromates are obtained by treating ammonium chromates with HNO_3 Aq. (For more details *v. abstract in C. J.* 56, 1117 [1889].) Various double compounds of

$(\text{NH}_4)_3\text{Cr}_2\text{O}_7$ with HgCl_2 are described by J. a. K. (*l.c.*).

Ceric dichromate $\text{CeO}_2 \cdot 2\text{Cr}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$. Prepared by passing a current of 2.5 to 3 volts through a slightly acid solution formed by dissolving $\text{Ce}_2(\text{SO}_4)_3$ in CrO_3 Aq.; insoluble water; boiling water forms yellow $\text{Ce}(\text{CrO}_4)_2$, and then $\text{CeO}_2 \cdot x\text{H}_2\text{O}$ (Bricout, *C. R.* 118, 145 [1894]).

Lead chromates. For double compounds of PbCrO_4 with Li_2CrO_4 , K_2CrO_4 , and Na_2CrO_4 , *v. Lachaud a. Lepierre, C. R.* 110, 1035 (*abstract in C. J.* 58, 1065 [1890]).

Mercury chromates. For basic mercuric chromates and a double compound of HgCrO_4 with NH_4HgCl *v. Jäger a. Krüss, B.* 22, 2028 (*abstract in C. J.* 56, 1120 [1889]).

Potassium chromates. Jäger *a. Krüss (l.c.)* prepare potassium trichromate $\text{K}_2\text{Cr}_2\text{O}_7$ by treating $\text{K}_2\text{Cr}_2\text{O}_7$ with HNO_3 Aq. S.G. 1.19, pouring off from KNO_3 that separates, and crystallizing; S.G. 2.648 at 11°. $\text{K}_2\text{Cr}_2\text{O}_7$ is quickly decomposed by water to CrO_3 Aq. and K_2CrO_4 Aq.; melts at 250°. Potassium tetrachromate $\text{K}_4\text{Cr}_2\text{O}_7$ is prepared by J. a. K. (*l.c.*) by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$ in hot conc. HNO_3 Aq. S.G. 1.41; S.G. 2.649 at 11°; not deliquescent; decomposed by water; crystallizes unchanged from HNO_3 Aq. S.G. 1.41. Schmidt (*B.* 25, 2917 [1893]) says that no nitrochromate is obtained by the action of HNO_3 Aq. on $\text{K}_2\text{Cr}_2\text{O}_7$; the substances obtained by Darmstädter (*v. vol. ii. p. 158*) were mixtures of KNO_3 and $\text{K}_2\text{Cr}_2\text{O}_7$.

Silver chromates. Pure silver chromate Ag_2CrO_4 is prepared by J. a. K. (*l.c.*) by repeatedly boiling Ag_2CrO_4 with water as long as anything dissolves; it is a deep-green solid, insol. water.

Sodium perchromate. Häussermann (*J. pr.* [2] 48, 70; *abstract in C. J.* 64 [11], 471) describes a salt $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{Na}_2\text{O}$, prepared by adding Na_2O_2 to a thin paste of CrO_3 H, and water, kept at 10°–20°.

Thallium chromates. For preparation of Tl_2CrO_4 and the double compound $\text{Tl}_2\text{CrO}_4 \cdot \text{K}_2\text{CrO}_4$, *v. Lachaud a. Lepierre, Bl.* [3] 6, 232 (*abstract in C. J.* 62, 467 [1892]).

Uranium chromates. For double uranyl chromates *v. Formánek, A.* 257, 102 (*abstract in C. J.* 58, 852 [1890]).

IODOCHROMATES (vol. ii. p. 157). A series of salts of the forms $\text{IO}_3 \cdot \text{O} \cdot \text{CrO}_3 \cdot \text{OM}^+$ and $(\text{IO}_3 \cdot \text{O} \cdot \text{CrO}_3 \cdot \text{O}) \cdot \text{M}^{++}$ has been obtained by Berg (*C. R.* 101, 1511 [1887]; 111, 42 [1890]); $\text{M}^+ = \text{NH}_4^+$, Li^+ , K^+ , Ag^+ , and Na^+ ; $\text{M}^{++} = \text{Co}$, Cu , Mg , and Ni . Most of the alkali salts were formed by dissolving the alkali iodate in excess of CrO_3 Aq. and crystallizing; the other salts were usually prepared by dissolving the oxide or carbonate of the metal in excess of CrO_3 Aq. and adding HIO_3 Aq. (For details *v. abstracts in C. J.* 55, 970 [1887]; 58, 1378 [1890].)

PHOSPHOCHROMATES. By adding conc. H_3PO_4 Aq. + CrO_3 Aq. to K_2CO_3 Aq. Blondel (*C. R.* 115, 194; *abstract in C. J.* 66 [11], 193 [1894]) obtained compounds of the form $m\text{K}_2\text{O} \cdot n\text{P}_2\text{O}_5 \cdot p\text{CrO}_3 \cdot x\text{H}_2\text{O}$, *m* being 2 and 3, *n* 4 and 8, and *x* being 0 or 1.

SULFOCHROMATES. In 1882 Cross *a. Higginf.* described a compound of Cr_2O_3 , SO_3 , and H_2O (*C. J.* 51, 113), and also compounds of CrO_3 , SO_3 , K_2O and H_2O . Recoura (*C. R.* 114, 477

- [1892]: 116, 1367; 117, 37, 101 [1893]) has made a more complete examination of these and allied compounds. By evaporating, at 100°, solutions containing violet $\text{Cr}_2(\text{SO}_4)_3$ and H_2SO_4 in the molecular ratio 1:1, 1:2, and 1:3, he obtained chromosulphuric acid $\text{H}_2\text{Cr}_2(\text{SO}_4)_4$, chromodisulphuric acid $\text{H}_2\text{Cr}_2(\text{SO}_4)_3$, and chromotrisulphuric acid $\text{H}_2\text{Cr}_2(\text{SO}_4)_2$; by using various sulphates in place of H_2SO_4 , he obtained chromosulphates, chromodisulphates, and chromotrisulphates. The acids are green powders, easily sol. water; they gradually decompose in solution; dilute BaCl_2 aq. ppt. Ba chromosulphates, but conc. BaCl_2 aq. gives BaSO_4 . R. obtained chromopyrosulphuric acid $\text{Cr}(\text{OH})(\text{S}_2\text{O}_4\text{H})$, by evaporating a solution of $\text{Cr}(\text{SO}_4)_3$ and H_2SO_4 in the molecular ratio 1:5, at 100°, and heating the dark-green syrupy liquid so obtained to 140–115° for some days. The acid forms brittle, transparent, pale-green laminae. Salts of the form $\text{Cr}(\text{S}_2\text{O}_4)_2(\text{OM})_2$ are obtained by adding alkalis to the acid in solution; these salts R. calls pyrosulphochromites. By adding conc. HCl aq. or H_2SO_4 to a solution of chromopyrosulphuric acid, R. obtained a compound $\text{Cr}_2(\text{OH})(\text{S}_2\text{O}_4)_2$, pyrosulphochromic hydrochloride, isomeric with chromosulphuric acid $\text{Cr}_2(\text{SO}_4)_2\text{H}_2$. (For more details v. abstracts in *C. J.* 62, 783 [1892]; 64 [11], 470, 528 [1893].)
- **COBALT**, vol. ii. p. 247. Winkler has re-determined at. w. of Co, (1) by dissolving electrolytically deposited Co in HCl aq., evaporating to dryness, and determining Cl in the CoCl_2 obtained (*Zeit. f. anorg. Chemie*, 4, 10 [1893]); (2) by finding the quantity of Ag deposited from solution of Ag_2SO_4 by electrolytically deposited Co (l.c. p. 462). The values obtained were 59.1 about 59.6 ($\text{Ag} = 107.66$).
- Alleged decomposition of cobalt.* Krüss a. Schmidt (*B. 22*, 11, 2026 [1889]) supposed they had separated Ni into two constituents, (r. vol. iii. p. 500); and they thought that Co also was probably not a homogeneous substance. Remmler, in 1893, obtained a number of specimens of Co_2O_3 , by ppg. CoCl_2 aq. ly. KOH aq. and Br water, treating the pp. with NH_4Ag , which gradually dissolves it, decanting off the ammoniacal solution at intervals during 9 months, evaporating each and heating in CO_2 ; the different specimens of Co_2O_3 were heated in H, and the quantity of Co obtained in each case was determined. The values thus obtained for the at. w. of Co varied from 59.53 to 58.3. R. concluded that Co purified by the ordinary methods is not a homogeneous substance. Winkler's determinations of the at. w. (v. *supra*), however, gave very constant values.
- *Reactions.*—Heated in NO to 750°, CoO is formed (Sabatier a. Senderens, *C. R.* 114, 1420 [1892]); finely divided Co burns in NO_2 at the ordinary temperature, giving Co_2O_3 ; but if H_2O NO_2 is largely diluted with N, a black compound is formed, Co_2NO_2 , called by S. a. S. (*C. R.* 115, 236 [1892]) *nitro-cobalt*. This compound reacts rapidly with H_2O , giving off NO , and forming a solution containing $\text{Co}(\text{NO}_2)_2$, with a very little $\text{Co}(\text{NO}_3)_2$, Co remaining insoluble, and sometimes also a basic nitrite; when heated in N_2 oxides of N are given off and then rapid decomposition occurs with formation of Co and oxides of Co, when mixed with combustible substance, Co_2NO_2 explodes (S. a. S., *l.c.* [1893]). Montemartini (*G. 22* [1], 250) finds that the gases produced by the interaction of Co and excess of HNO_3 aq. (27.5 p.c.) are NH_3 , N_2O , and N (v. abstract in *C. J.* 62, 1278 [1892]).
- Cobalt chloride** (vol. ii. p. 219). For the solubility of CoCl_2 in water, and the changes of colour produced by digesting the solution, with a discussion of the hydrations and dehydrations that accompany these changes, v. Etard, *C. R.* 113, 609 (abstract in *C. J.* 62, 378 [1892]); Engel, *Bl.* [3] 239 (abstract in *C. J.* 62, 569 [1892]); and Potilitzin, *Bl.* [3] 6, 264 (abstract in *C. J.*, l.c. p. 571). The double compounds $\text{CoCl}_2 \cdot \text{HCl}$ 3aq., $\text{CoCl}_2 \cdot \text{LiCl}$ 3aq., and $\text{CoCl}_2 \cdot \text{NH}_4\text{Cl}$ 6aq. are described by Chassevant (*J. Ch.* [6] 30, 5 [1893]).
- Cobalt fluoride** (vol. ii. p. 220). Pouleno (*C. R.* 114, 1426; v. abstract in *C. J.* 62, 1159 [1892]) prepares CoF_3 by heating CoF_2 with excess of NH_4F for 15 minutes, and repeatedly washing the double fluoride $\text{CoF}_2 \cdot 2\text{NH}_4\text{F}$ thus obtained with boiling alcohol. By heating CoF_2 to 1200–1300° in HF , the salt is obtained in small, rose-red prisms; S.G. 4.13. The double compound $\text{CoF}_2 \cdot 2\text{KF}$ is formed by heating CoCl_2 with KHF_2 (P., l.c. p. 746; abstract, l.c. p. 781).
- Cobalt iodide** (vol. ii. p. 220). For solubility in water of CoI_2 , and the formation of various hydrates attending solution, v. Etard, *C. R.* 113, 609 (abstract in *C. J.* 62, 278 [1892]).
- Cobaltous oxide** CoO (vol. ii. p. 220). This oxide melts in the electric furnace, and forms rose-coloured crystals (Moissan, *C. R.* 115, 1034 [1892]).
- Cobaltous hydroxide** $\text{CoO} \cdot \text{H}_2\text{O}$ (vol. ii. p. 220). A. de Schulten (*C. R.* 109, 266 [1889]) obtained this compound in microscopic, brownish-red, four-sided prisms, S.G. 3.597 at 15°, by heating 10 g. CoCl_2 6aq. in 60 c.c. water with 250 g. KOH , in a flask filled with coal-gas, letting stand for 24 hours, and washing away the lighter amorphous products of the reaction.
- Cobalto-cobaltic oxides** (vol. ii. p. 221). Regarding Co_2O_3 and oxides intermediate between this and Co_3O_4 , v. Schröder, *C. C.* 1890, [1] 931 (abstract in *C. J.* 58, 1213 [1890]). Co_2O_3 heated to c. 1750° loses all its O, and leaves Co (Read, *C. J.* 65, 313 [1891]).
- Cobalt, dioxide of.** By the reaction of IAg and NaOH aq. on CoSO_4 aq., filtering, and acidifying with acetic acid, Vortmann (*B. 24*, 2741, abstract in *C. J.* 60, 1429 [1891]) obtained a greenish-black pp. nearly agreeing with the formula Co_2O_3 . For compounds of Co_2O_3 with BaO v. Rousseau, *C. R.* 107, 614 (abstract in *C. J.* 56, 1115 [1889]).
- Cobalt, salts of** (vol. ii. p. 221). Marshall (*C. J.* 59, 760 [1891]) has prepared the salts $\text{Co}_2(\text{NO}_2)_4$, 18aq. and $\text{Co}_2(\text{C}_2\text{O}_4)_3 \cdot 3(\text{NH}_4)_2\text{C}_2\text{O}_4$ 6aq. by electrolyzing a solution of CoSO_4 in H_2SO_4 aq., and of Co_2O_3 aq. containing $(\text{NH}_4)_2\text{C}_2\text{O}_4$.
- COBALTAMMINES** (vol. ii. p. 222). By cryoscopic determinations, Petersen (*Z. P. C.* 10, 580 [1892]) concludes that the formulae generally given to the chief cobaltamines are molecular. For a discussion of the constitution of these compounds, v. Jørgensen (*J. pr.* [2] 41, 429, 440 [1890]; 42, 206; 45, 274 [1891–92]). For various octamines, v. Vortmann a. Blasberg (*B. 22*, 2649), and V. a. Magdeburg (*B. 22*,

2680; *abstracts in C. J.* 58, 14 [1890]. V. a. Morgulis (*B.* 23, 2644; *abstract in C. J.* 58, 13 [1890]), describe several *mercuricobaltammines*. A number of *croceo-, luteo-, and xantho-salts*, and also several *flavo-salts* isomeric with the *croceo-salts*, are described by Jørgensen in *Zeit. f. anorg. Chemie*, 5, 147 (*abstract in C. J.* 65 [11], 50 [1894]).

COPPER (vol. ii. p. 251). An elaborate investigation of the at. w. of Cu has been made by Richards, *P. Am. A.* 26, 240 [1891] (*v. C. N.* 65, 236, &c.; *abstract in C. J.* 64 [11], 12 [1893]). $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was analysed and synthesised, and CuO was analysed; the final value obtained by R. is 63.604 ($Q = 16$), or 63.44 ($Q = 15.96$). The molecule of Cu in dilute solution in tin is probably monatomic (Heycock & Neville, *C. J.* 57, 376 [1890]). For the absorption spectra of solutions of CuCl_2 , CuSO_4 , and $\text{Cu}(\text{NO}_3)_2$, v. Evan, *P. M.* [5] 83, 817 (*abstract in C. J.* 64 [11], 149 [1893]).

Preparation.—For the preparation by electrolysis of pure copper v. Richards (*P. Am. A.* 25, 199, 206 [1890]).

Reactions.—Heated in the electric furnace, using a current of 70 volts and 350 amperes, Cu rapidly volatilises, and the vapour forms CuO in the air (Moissan, *C. R.* 116, 1429 [1893]). According to Neumann (*M.* 13, 40 [1893]), the H occluded in Cu prepared by reducing CuO by H, cannot be wholly expelled by heating in a stream of CO_2 ; some of the CO_2 is also absorbed by the Cu. N. also says that Cu reduced by vapour of MeOH or EtOH , or by coal gas, retains very small traces of C and H after being heated to 220° . Montemartini (*G.* 22, 284, 377, 426 [1892]) says that the reaction between Cu and HNO_3 aq. of less than 30 p.c. produces $\text{Cu}(\text{NO}_3)_2$ and HNO_2 , the HNO_2 then decomposing to HNO , NO , and H_2O ; with acid more conc. than 30 p.c. HNO_3 some NO_2 is produced with a little N_2O , and with 70 p.c. acid only NO is given off; no appreciable quantity of NH_3 is produced with acid from 3 to 27.5 p.c. HNO_3 . According to Freer & Higley (*Am.* 15, 71 [1893]), the only gaseous products of the reaction of Cu with excess of HNO_3 aq. S.G. 1.4 (c. 65 p.c. HNO_3) are NO_2 and N_2O , c. 90 p.c. NO_2 and 10 p.c. N_2O . Cu is superficially oxidised in NO at a dull red heat (Sabatier & Senderens, *C. R.* 114, 1429 [1892]). Reduced Cu absorbs NO_2 at the ordinary temperature, forming a brownish powder Cu_2NO_2 (S. a. S., *C. R.* 115, 236 [1892]). For the reactions of this nitro-copper v. S. a. S., *C. R.* 116, 756 (*abstract in C. J.* 64 [11], 874 [1893]).

Copper, alloys of (vol. i. p. 253). For a description of alloys of Cu with O_2 , Sn, and Zn, prepared by immersing plates of Cd, Sn, or Zn, in solutions of salts of Cu, v. Mylius & Fromm, *B.* 27, 840 (*abstract in C. J.* 66 [11], 235 [1894]).

Cupric bromide (vol. ii. p. 254). According to Sabatier (*C. R.* 118, 980 [1891]), the green crystals that separate from CuBr_2 aq. are $\text{CuBr}_2 \cdot 2\text{aq}$. A solution of CuBr_2 in conc. HBr aq. has an intense purple colour which becomes less marked on dilution, but even with .0015 mgm. Cu in solution the colour can be detected (S., *l.c.*) The double salts $\text{CuBr}_2 \cdot \text{CsBr}$ and $\text{CuBr}_2 \cdot 2\text{CsBr}$ are described by Wells & Walden

(*Zeit. f. anorg. Chem.*, v. 304; *abstract in C. J.* 66 [11], 47 [1894]).

Cupric chloride (vol. ii. p. 255). Tsuchanoff (*J. R.* 25, 151; *abstract in C. J.* 66 [11], 47 [1894]) finds that the E.C. of dilute blue-coloured CuCl_2 aq. increases with increase of concentration to a maximum, after which it decreases while the colour changes to yellowish-brown. For heats of solution and dilution of CuCl_2 2aq. v. Reichert & Deventer (*Z. P. C.* 5, 559 [1890]).

Double salts.— $\text{CuCl}_2 \cdot \text{HCl}$ 3aq, $\text{CuCl}_2 \cdot \text{LiCl}$ 2aq, $\text{CuCl}_2 \cdot \text{NH}_4\text{Cl}$, $\text{CuCl}_2 \cdot 2\text{NH}_4\text{Cl}$ 2aq, $\text{CuCl}_2 \cdot \text{KCl}$, and $\text{CuCl}_2 \cdot 2\text{KCl}$ 2aq (Chassevant, *Ch.* [6] 80, 5 [1893]); $\text{CuCl}_2 \cdot \text{CsCl}$, $\text{CuCl}_2 \cdot 2\text{CsCl}$ 2aq ($x = 0$ and 2), and $2\text{CuCl}_2 \cdot 3\text{CsCl}$ (Wells & Dupree, *Zeit. f. anorg. Chemie*, 5, 800 [1893]).

Cuprous chloride (vol. ii. p. 255). Wells (*l.c.*, p. 306) describes the double salts $2\text{CuCl} \cdot \text{CsCl}$, $2\text{CuCl} \cdot 3\text{CsCl}$, and $\text{CuCl} \cdot 3\text{CsCl}$ aq.

Cupric fluoride (vol. ii. p. 256). Poulenc (*C. R.* 116, 1446; *abstract in C. J.* 64 [11], 525 [1893]) prepares CuF_2 , as a white amorphous powder, by heating NH_4F with CuF_2 2aq; by heating in HF at 500° (not above) the CuF_2 becomes crystalline. Crystalline CuF_2 is also obtained by heating CuO , or CuF_2 2aq, in HF at 400° (P., *l.c.*). Heated to 800° in air CuO is formed; heating in steam gives CuO and HF ; H_2S forms CuS and HF ; HCl forms CuCl_2 . CuF_2 absorbs water from the air, and becomes blue. H. von Helmholtz (*Zeit. f. anorg. Chemie*, 3, 115 [1892]) describes the double salts $\text{CuF}_2 \cdot \text{KF}$, $\text{CuF}_2 \cdot \text{RbF}$, $\text{CuF}_2 \cdot \text{AmF}$ 2aq, and $\text{CuF}_2 \cdot 2\text{AmF}$ 2aq.

Cuprous fluoride (vol. ii. p. 256). According to Mauro (*Real. Acad. Lincei*, 1892 [L], 194; *abstract in C. J.* 64 [11], 124 [1893]), Cu_2F_2 does not exist, and the substance obtained by Berzelius was almost certainly merely impure copper. Poulenc, however (*C. R.* 116, 1446; *abstract in C. J.* 64 [11], 525 [1893]), says that Cu_2F_2 is formed by heating Cu_2Cl_2 to dull redness in HF (the action is not complete until 1100° – 1200°); also by heating CuF_2 in HF at c. 600° , raising the temperature to 1100° – 1200° towards the end of the reaction. P. describes Cu_2F_2 that has been fused as a ruby-red, transparent solid, with a crystalline fracture; exposed to moist air it changes to CuF_2 2aq; it is easily reduced by H at a red heat.

Cuprous iodide (vol. ii. p. 256). Brun (*C. R.* 114, 667; *abstract in C. J.* 62, 1157 [1893]) describes double compounds with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and NH_4I , and also with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and $\text{Cu}_2\text{S}_2\text{O}_8$.

Cuprous oxide (vol. ii. p. 258). Russell (*C. N.* 62, 308 [1893]) prepares Cu_2O by completely reducing Cu_2NO aq. mixed with excess of NaCl by SO_2 , heating till excess of SO_2 is removed, and then ppg. by Na_2CO_3 , added solid to the hot solution. With HFA aq, CuF_2 aq and Cu are formed (Poulenc, *C. R.* 116, 1446 [1893]).

Cupric oxide (vol. ii. p. 258). Moissan (*C. R.* 115, 1034 [1892]) says that CuO is entirely decomposed in the electric furnace at c. 2500° , yielding Cu and a crystalline compound of CuO and CaO (the reaction was effected in a block of CaO). By heating CuO to whiteness, in a Fletcher injector-furnace, in an oxidising atmosphere, Bailey & Hopkins (*C. J.* 57, 269 [1890]) obtained a very hard, yellowish-red

- solid agreeing with the formula Cu_2O . Richards (P. Am. A. 26, 281 [1891]) found that CuO excludes gas, chiefly N; when prepared by heating $\text{Cu}(\text{NO}_3)_2$, the oxide retained c. .08 p.c. of its weight of N, which could not be removed by heating. For experiments on the dehydration of $\text{CuO} \cdot x\text{H}_2\text{O}$ v. Spring a. Lucion (Zeit. f. anorg. Chemie, 2, 195; abstract in C. J. 64 [11], 210 [1893]). For colloidal, jelly-like $\text{CuO} \cdot x\text{H}_2\text{O}$ v. J. van Bemmelen (Zeit. f. anorg. Chemie, 5, 466; abstract in C. J. 65 [11], 191 [1894]).
- Copper, oxybromides** of (vol. ii. p. 260). Dupont a. Jensen (Bl. [3] 9, 193; abstract in C. J. 64 [11], 463 [1893]) obtained the salt $3\text{CuO} \cdot \text{CuBr}_2 \cdot 3\text{aq}$ by heating $\text{CuBr}_2 \cdot \text{aq}$ with CuO in a sealed tube at 200° , or, better, by heating neutral dilute $\text{CuBr}_2 \cdot \text{aq}$ at 225° ; the compound crystallised in green rhombohedral plates, S.G. 4.39.
- Copper, oxychlorides** of (vol. ii. p. 260), v. Roussseau, C. R. 110, 1261 (abstract in C. J. 58, 1058 [1890]).
- Copper, oxysulphides** of (vol. ii. p. 260), v. Cliche, Ar. Ph. 228, 374 (abstract in C. J. 58, 1211 [1890]).
- Copper, phosphides** of (vol. ii. p. 260). For descriptions of Cu_3P_2 and Cu_2P , prepared by heating Cu in vapour of P, v. Granger, C. R. 113, 1401; and for Cu_3P_2 , prepared by heating red P with excess of Cu phosphite and water, v. G., C. R. 117, 237 (abstracts in C. J. 62, 410 [1892]; and 64 [11], 526 [1893]).
- Cupric sulphide**. From experiments on the interaction of H_2S and $\text{CuSO}_4 \cdot \text{aq}$ and CuSO_4 in presence of acetic acid, Linder a. Pictet (C. J. 61, 120 [1892]) conclude that a compound $7\text{CuS} \cdot \text{H}_2\text{S}$ is formed, and that then such compounds as $9\text{CuS} \cdot \text{H}_2\text{S}$ and $22\text{CuS} \cdot \text{H}_2\text{S}$ are produced, and finally $(\text{CuS})_n$ is formed.
- COPPER-AMMONIUM COMPOUNDS** (vol. ii. p. 262). Several derivatives of cuprammonium bromide are described by Richards a. Shaw (P. Am. A. 28, 247 [1893]).
- FERRICYANIDES**.
- Barium ferricyanide** (vol. ii. p. 337); v. Rammelsberg, J. pr. [2] 39, 455 (abstract in C. J. 56, 950 [1889]).
- Lead ferricyanide** (vol. ii. p. 330); v. Rammelsberg (l.c.).
- Potassium ferricyanide** (vol. ii. p. 330); v. Kassner, Chem. Zeit. 13, 1701 (abstract in C. J. 58, 352 [1890]).
- DIDYMIUM** (vol. ii. p. 382). For an investigation into the separation of Di and Er, v. Krüss, A. 265, 1 (abstract in C. J. 65, 1421 [1891]). For the emission spectra of oxides of neodymium and praseodymium, v. Haitinger, M. 12, 362 (abstract in C. J. 62, 2 [1892]). Read (C. J. 65, 313 [1891]) says that Di_2O_3 is unchanged at c. 1750° .
- ERBIUM** (vol. ii. p. 456). For the separation of compounds of Er and Di, v. Krüss, A. 265, 1 (abstract in C. J. 60, 1424 [1891]).
- FERRITES** (vol. ii. p. 547). J. van Bemmelen a. Hobbs (J. pr. [2] 46, 497 [1892]) say that $\text{FeO} \cdot \text{K}_2\text{C}$ and $\text{FeO} \cdot \text{Na}_2\text{O}$ are obtained, in crystals, by continued heating Fe_2O_3 with conc. KOHaq and NaOHaq respectively; these ferrites are decomposed by water, giving $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$.
- FLAME** (vol. ii. p. 549). Reference should be made to Smithells a. Ingle on 'The Structure and Chemistry of Flames' in C. J. 61, 204 [1892], and to Lewes on 'The Luminosity of Coal-gas Flames' in ibid. p. 322.
- FLUORHYDROIC ACID** (vol. ii. p. 558). Berthelot a. Moissan (C. R. 109, 209 [1889]) give the thermal data $[\text{H.F.}] = 37,600$; $[\text{H.F.Aq}] = 49,400$. For the description of an apparatus for purifying HFAq , v. Hquilton (C. N. 60, 252 [1889]).
- FLUORINE** (vol. ii. p. 560). Moissan (C. R. 111, 370 [1890]) determined the at. w. (1) by converting $\text{Na}_2\text{C}_2\text{O}_4$ into NaF , and this into Na_2SO_4 ; (2) by converting CaF_2 into CaSO_4 , and (3) by converting BaF_2 into BaSO_4 ; the mean of the results regarded by M. as the most trustworthy was 19.05. V.D. at the ordinary temperature, 18.3 (Moissan, C. R. 109, 861; v. abstract in C. J. 58, 208 [1890]). A column of F one metre long shows no definite absorption bands (M., l.c. p. 937); for the emission spectrum v. M. (l.c., abstract in C. J. 58, 329 [1890]). F does not liquefy at -95° at the ordinary pressure (M., A. Ch. [6] 25, 125 [1893]). Gladstone (P. M. [5] 31, 1 [1891]) has determined the atomic refraction of F in $\text{O}_2\text{H}_2\text{F}$ to be as follows for the different lines of the solar spectrum, at 22.8° :—
- | | A | C | D | E | F | G | H |
|----------------|-----|-----|-----|-----|-----|-----|---|
| at. refraction | .63 | .63 | .53 | .48 | .44 | .35 | |
- The values are much smaller than those for Cl, Br, or I, which are 10.0, 15.23, and 25.2 for the line A.
- Formation**.—According to Brauner, (C. J. 65, 393 [1891]), F is given off when $3\text{KF} \cdot \text{PbF}_2 \cdot \text{HF}$ (v. LEAD TETRAFLUORIDE, p. 145) is heated to dull redness.
- Reactions**.—F combines with the more porous forms of carbon at the ordinary temperature, with incandescence, forming CF_4 ; the denser forms of C combine with incandescence at from 50° to 100° (Moissan, C. R. 110, 276; abstract in C. J. 58, 557 [1890]). For a discussion of the chemical relations of F, v. Moissan, Bl. [3] 5, 880 [1891].
- GALLIUM** (vol. ii. p. 597). Lecocq de Boisbaudran (C. R. 114, 815; abstract in C. J. 62, 930 [1892]) gives measurements of the chief lines in the spark emission spectrum of Ga; the spectrum varies much according to the conditions under which the spark is applied.
- GERMANIUM** (vol. ii. p. 610). A new mineral from Bolivia, *argyrodite*, Ag_2GeS_4 , identical in composition with *argyrodite* from Freiberg, but crystallising in isometric forms (the form of *argyrodite* is monoclinic), is described by Field in Am. S. [3] 46, 107 (abstract in C. J. 66 [11], 19 [1894]).
- GOLD** (vol. ii. p. 647). Melet (Pr. 46, 71; abstract in C. J. 58, 708 [1890]) has re-determined the at. w. of gold by various methods; the mean value obtained is 196.9, but the value 196.88 M. thinks is more trustworthy. The molecule of gold in dilute solution in this is probably monatomic (Heycock a. Neville, C. J. 57, 376 [1890]). Gold volatilises considerably in the electric furnace with a current of 70 volts and 360 amperes (Moissan, C. R. 116, 1429 [1892]).

Concerning the volatilisation of gold v. Rose (*C. J.* 63, 714 [1893]). Neumann (*M.* 13, 40 [1892]) says that gold absorbs from 33 to 46.5 times its volume of O at 450° . According to Petersen (*Z. P. C.* 8, 601 [1892]), the heats of formation of Au_2O_3 from gold (1) reduced from AuCl_3 , (2) from AuHBr_2 , and (3) from AuBr , differ very markedly. From the results of many experiments on the reaction between gold and KCN aq. Maclaurin (*G. J.* 63, 724 [1893]) concludes that O must be present to accomplish solution, and that the equation $4\text{Au} + 8\text{KCN} + \text{O}_2 + 2\text{H}_2\text{O} = 4(\text{AuCN.KCN})\text{Aq} + 4\text{KOH}$ aq. (Elsner, *J. pr.* 37, 323 [1849]) expresses the proportion between K and Au in the solution.

Gold alloys (of vol. ii. p. 648). For an alloy with Cd, AuCd, v. Heycock & Neville (*G. J.* 61, 914 [1892]). For alloys with Cd and Sn, v. H. a. N. (*C. J.* 59, 936 [1891]). For alloys with Al and Sn, Cd and Bi, Cd and Pb, and Cd and Ti, v. H. a. N. (*C. J.* 65, 65 [1894]). For alloys with Cd and Zn, prepared by immersing plates of Cd and Zn in solution of a salt of gold, v. Mylius a. Fromm (*B.* 27, 630; abstract in *C. J.* 66 [11], 235 [1894]).

Gold bromides (of vol. ii. p. 648). Petersen (*J. pr.* [2] 46, 328) upholds the existence of AuBr , against the statements of Krüss a. Schmitt (*B.* 20, 244); in a later paper (*J. pr.* [2] 47, 301) K. a. S. still maintain that AuBr_2 is the ultimate product of the reaction of Br with gold (v. abstracts in *C. J.* 64 [11], 126, 284). For the double salts AuBr_2 , CsBr and AuBr_2 , RbBr , v. Wells a. Wheeler (*Am. S.* [3] 44, 157 [1892]).

Gold chlorides (of vol. ii. p. 649). Petersen (*G. pr.* [2] 46, 328; 48, 88) maintains that AuCl_2 is a definite compound; Krüss a. Schmitt (*J. pr.* [2] 47, 301; *Zeit. f. anorg. Chemie*, 3 421) say this substance is a mixture (v. abstracts in *C. J.* 64 [11], 126, 284, 474 [1893]).

Double salts of AuCl_2 with CsCl and RbCl are described by Wells a. Wheeler (*l.c.*); for a double salt AuCl_2 , AgCl , v. Hermann (*B.* 27, 596; abstract in *C. J.* 66 [11], 234 [1894]).

Gold sulphides (of vol. ii. p. 651). Concerning the conditions of formation of Au_2S , v. Antony a. Lucchesi (*G.* 19, 545; abstract in *C. J.* 58, 1216 [1890]).

Auric sulphide Au_2S_3 . This compound is formed, according to A. a. L. (*G.* 20, 601; 21 [11], 209; abstracts in *C. J.* 60, 526; 62, 430 [1892]), by passing H_2S into a solution of AuCl_3 , LiCl kept at -10° , extracting LiCl by absolute alcohol, and drying in N at 70° . Au_2S_3 is a black, amorphous solid; decomposed by heat at 200° – 205° to Au and S (for other reactions v. abstracts, *l.c.*).

Schneider (*U. S. Geol. Survey Bull.* No. 90, 56, [1892]) obtained aqueous solutions of colloidal Au_2S and Au_2S_3 .

HYDRAZONIC ACID (v. p. 919, Addenda).

HYDROGEN (vol. ii. p. 719). The ratio between the densities of H and O is 1:15.832; the weight in grams of 1 litre of H is .08991 (Rayleigh, *Phil. Mag.*, 134 [1893]). For solubility in water, and in alcohol, v. Timofeff (*Z. P. C.* 6, 141); Winkler (*B.* 24, 89); Henrich (*Z. P. C.* 9, 435); (abstracts in *C. J.* 60, 15, 384 [1891]; 62, 1043 [1892]). For the line spectrum of H, v.

Anges (*Z. M.* [5] 30, 48 [1890]); and cf. Grünwald (*M.* 13, 111; abstract in *C. J.* 62, 1381 [1892]).

Wilm (*B.* 25, 217; abstract in *C. J.* 62, 563 [1892]) describes a lecture experiment to show the occlusion of H by Pd. Regarding the occlusion of H by other metals v. Streintz (*M.* 12, 642; abstract in *C. J.* 62, 567 [1892]).

Baker (*C. J.* 65, 611 [1894]) found that a mixture of equal volumes of dry H and dry Cl did not explode in bright sunlight, and that more than a quarter of the mixed gases remained uncombined after exposure for two days to diffused light and two days to bright sunshine.

Reactions.—Neumann (*Z. P. C.* 14, 193 [1894]) has examined the reducing action of H occluded by Pt on solutions of salts of Al, Sb, As, Bi, Cd, Cu, Co, Au, Fe, Pb, Mg, Mn, Hg, Ni, Pd, Ag, Sn, Ti, and Zn. Regarding the rate of combination of H and O, v. WATKIN (p. 860). Regarding the explosion of mixtures of H with O and Cl, v. CHLOPINE (*Addenda*, pp. 904, 905).

Hydrogen dioxide (vol. ii. p. 722). Schöne (*B.* 26, 3011; 27, 1233 [1893–4]) affirms the occurrence of H_2O_2 in the atmosphere against the contention of Ilsva (*B.* 27, 920).

Formation.—Regarding the formation from ether v. Dunstan a. Dymond (*C. J.* 57, 574, 988 [1890]). H_2O_2 aq. is formed by the action of light on $\text{H}_2\text{C}_2\text{O}_4$ aq. excess of O being present (Richardson, *C. J.* 65, 450 [1894]). Richardson (*C. J.* 63, 1110 [1893]) has examined the formation of H_2O_2 in urine exposed to sunlight.

Preparation.—By making commercial 3 p.c. H_2O_2 aq. distinctly alkaline by Na_2CO_3 , filtering, soaking with 10–12 vols. of ether, separating the ethereal solution, evaporating this to .01–.0025 of its original volume on a water-bath, and removing the rest of the ether by standing in a bell-jar over solid paraffin, Shiloff (*J. R.* 25, 293; abstract in *C. J.* 66 [11], 186 [1894]) obtained a thick, transparent, slightly acid liquid, S.G. 1.2475, containing 79.6 g. H_2O_2 in 100 c.c. For preparation of conc. H_2O_2 aq. v. Talbot a. Moody (abstract in *C. J.* 64 [11], 369 [1893]).

Molecular weight. Tamman in 1889 (*Z. P. C.* 4, 441) by cryoscopic measurements determined mol. formula to be H_2O_2 ; but T.'s results were called in question by Carrara in 1893 (*G. Z.* 22 [1], 341), who found mol. w. 33.92 (H_2O_2) from cryoscopic measurements, and this result was confirmed by Orndorff a. White (*Am.* 15, 342 [1893]), and also by Tamman himself (*Z. P. C.* 12, 431 [1893]).

Reactions.—Regarding the reaction between H_2O_2 aq. and KMnO_4 aq. v. Engel (*B.* [3] 6, 17; abstract in *C. J.* 62, 277 [1892]).

Hydrogen sulphide (vol. ii. p. 725). Henrich (*Z. P. C.* 9, 435 [1892]) gives the absorption coefficient of H_2S by water as 4.4015–.089117 + .00061954t. Hughes (*P. M.* [5] 33, 471 [1892]) says that H_2S dried by CaCl_2 and P_2O_5 does not render dry litmus paper, and does not react with BaO or Fe_2O_3 , nor with salts of Sb, As, Bi, Cd, Co, Cu, Pb, Hg, Ag, or Sn. According to Pöller (*C. J.* 57, 625 [1890]), the equation $2\text{H}_2\text{S} + 3\text{O}_2 = 2\text{SO}_2 + 2\text{H}_2\text{O}$ correctly represents the explosion of H_2S and air or O .

HYDROXYLAMINE (vol. ii. p. 734). NH_2OH has been isolated as a solid by Schmitt.

(R. T. O. *U.*, 100; 11, 15, *abstracts in C. J.* 62, 402, 1891 [1892]). $\text{NH}_4\text{OH.HCl}$ dissolved in MeOH is treated with CH_3ONa solution, and most of the MeOH is distilled off at 100 mm. pressure; the residue is distilled in small portions at 40 mm. pressure (for details v. C. J., l.c.). For the preparation from $2\text{NH}_4\text{OH.ZnCl}_2$, v. Crismer, *Bl.* [3] 6, 793 (*abstract in C. J.* 62, 771 [1892]). For details of suitable apparatus for the fractionation of NH_4OH *in vacuo*, v. Brühl (*B.* 26, 2508 [1893]; cf. L. de B., *B.* 27, 307, and reply by Berthelot, *B.* 27, 307, 1894). For thermal data of NH_4OH , v. Berthelot & André (*C. R.* 110, 830; *abstract in C. J.* 58, 934 [1890]). Hydroxylamine is a white, odorless solid, melting at -33° , and remaining superheated at 0° ; boils at 58° under 22 mm. pressure; decomposes at 90° – 100° , and detonates at a higher temperature. S.G. 1.35; S.G. when liquid, 1.23. A drop heated in a test tube explodes very violently (v. Brühl, l.c.). B., l.c., discusses the molecular refraction of NH_4OH . NH_4OH is fairly stable up to 15° , then gradual decomposition occurs, giving NH_3 , HNO_2 , and $\text{H}_2\text{N}_2\text{O}_2$, which react with unchanged NH_4OH producing O and N_2 . L. de B., *B.* 27, 967, *abstract in C. J.* 66 [11], 278 [1891]). For a full account of the reactions of NH_4OH , v. Lobry de Bruyn (l.c.; *abstract in C. J.* 62, 1391 [1892]). $\text{H}_2\text{N}_2\text{O}_2$ in water and NaNO_2 aq. react to form NaNO_2 aq. (v. Tonnar, *J. R.* 25, 312; *abstract in C. J.* 66 [11], 136 [1891]; cf. Vislicenus, *B.* 26, 771; *abstract in C. J.* 64, 18 [1892]). For the reactions of $2\text{NH}_4\text{OH.H}_2\text{SO}_4$ with NaOHAq , v. Kolotoff (*J. R.* 25, 295; *abstract in C. J.* 66 [11], 187 [1891]). For compounds of NH_4OH with metallic salts, v. Crismer, *Bl.* [3] 8, 114; Goldschmidt & Syngros (*Z. anorg. Chemie*, 5, 129); and Feldt (*B.* 27, 401) (*abstracts in C. J.* 58, 558 [1890]; 66 [11], 15, 187 [1894]). Kolotoff discusses the constitution of NH_4OH in *J. R.* 23, 3 (*abstract in C. J.* 64 [11], 114 [1893]). Kjellin (*B.* 26, 2377) describes $\text{NH}_4\text{F.OH}$ and NHMe.OH (*abstract in C. J.* 66 [11], 9 [1894]).

INDIUM (vol. iii. p. 1). The molecule of indium in dilute solution in tin is perhaps diatomic (v. Heycock & Neville, *C. J.* 57, 376 [1890]). Linder & Picton (*C. J.* 61, 131 [1892]) failed to isolate *indium hydrosulphide*, but they think that it is formed by passing H_2S into water with In_2O_3 in suspension; the continued passage of H_2S produces In_2S_3 . Read (*C. J.* 65, 313 [1894]) found that *indium sesquioxide*, In_2O_3 , is unchanged at 675° .

IODHYDRIC ACID (vol. iii. p. 11). For the Mol. R. of HIAg from 20.77 to 67.92 p.c., v. Perkin (*C. J.* 55, 708 [1889]). For a research on the dissociation of HI , v. Rodenstein (*Z. P. K.* 33, 56 [1894]; *abstracts in C. J.* 61 [11], 369; 66 [11], 12 [1893-4]). Nickling (*B.* 26, 2007) has isolated three hydrates of HI : $\text{HI.2H}_2\text{O}$, melting at -43° ; $\text{HI.3H}_2\text{O}$, melting at -48° ; and $\text{HI.4H}_2\text{O}$, melting at -36.5° .

IODINE (vol. iii. p. 14). The mol. w. of iodine dissolved in Et_2O or CS_2 was found by Beckmann (*Z. A. C.* 5, 76 [1890]) to be 254, from determinations of the boiling-point; the results were confirmed by Sakurai (*C. J.* 31, 394 [1892]). By determining the lowering of the f.p. of naphthalene by solution therein of I_2 ,

Hertz (*Z. P. O.* 3, 358 [1890]) found the value 254 for the mol. w. of iodine.

According to Meineke (*Chem. Zeitung*, 10, 121, 1230), very pure I_2 is prepared by covering ordinary I_2 with a solution of CaCl_2 , S.G. 1.85, mixed with a little conc. KIAg and a few drops of HClAq , heating until the I_2 fuses, letting cool, washing the I_2 , drying, and subliming it twice, the first time with addition of a little BaO .

For the reactions of I_2 with KClO_3 , and with KClO_4 and water, v. POTASSIUM CHLORATE (*Addenda*, p. 905).

Iodine monochloride (vol. iii. p. 17). For thermal data bearing on the two forms of ICl , v. Stortenbecker (*Z. P. C.* 10, 183; *abstract in C. J.* 62, 1387 [1892]). Tannier (*J. R.* 25, 47; *abstract in C. J.* 64 [11], 514) gives details of the methods for preparing the two forms of ICl .

Iodates (vol. iii. p. 21). For *iodates of cesium* and *rubidium*, v. Wheeler, *Am. S.* [3] 44, 123 (*abstract in C. J.* 64 [11], 68 [1894]). Pure potassium iodate is prepared, according to Gröger (*Zeit. angew. Chemie*, 1891, 13), by heating to 100° for 20–30 minutes 20 g. KI in as little water as possible mixed with 40 g. pure KMnO_4 in 1,000 c.c. water, reducing excess of KMnO_4 by cautious addition of alcohol, filtering, adding acetic acid till acid, evaporating to c. 50 c.c., washing the crystals of KIO_3 with conc. alcohol, and drying. By heating KIO_3 till it fuses, O and some I_2 are given off, and K_2O finally remains; no other oxy-compounds are formed (Cook, *C. J.* 65, 802 [1894]).

IRIDIUM (vol. iii. p. 46). From analyses of the salts $\text{ICl}_3.3\text{KCl}$ aq. and $\text{ICl}_3.3\text{NH}_4\text{Cl}$ aq. Joly deduced the value 192.75 for the at. w. of Ir (*C. R.* 110, 1131 [1890]). According to Prinz (*C. R.* 116, 392 [1893]), Ir crystallises in regular octahedra and in forms derived therefrom. Milius & Foerster (*B.* 25, 665 [1892]) stated that Ir is slightly volatilised when heated in a current of CO and Cl_2 to c. 238° ; Antony, however (*G. Z.* [11], 547 [1893]), asserts that no trace of any volatile compound of Ir is formed under these conditions.

Irid-ammonium salts (vol. iii. p. 47). Palmae (*B.* 22, 15; 23, 3910 [1889-90]) describes a number of irido-ammonium compounds. He calls them *iridiumpentammine salts*, and formulates them as $\text{Ir}(\text{NH}_3)_5\text{X}_2$; compounds are described where $\text{X}_2 = \text{Cl}_2$, ClBr , ClI , ClSO_3 , $\text{Cl}(\text{NO}_2)$, $\text{Cl}(\text{NO}_2)_2$, ClC_2O_5 , $\text{ClP}(\text{Cl})_2$; also where $\text{X}_2 = \text{Br}$, BrSO_3 , and $\text{Br}(\text{NO}_2)$. One-third of the Cl in the salt when $\text{X}_2 = \text{Cl}_2$ is not removed by the action of cold H_2SO_4 aq. or cold AgNO_3 aq.; the reactions of the salts are similar to those of the purplecobaltammines (v. vol. ii. p. 227) (*abstracts in C. J.* 56, 252 [1889]; 60, 402 [1891]). In *B.* 21, 2090 (v. *abstract in C. J.* 60, 11 [1892]) P. describes compounds analogous with the purplecobaltic salts $\text{Co}(\text{NH}_3)_6(\text{H}_2\text{O})\text{X}_2$, as the I salts are almost colorless. P. thinks the prefix *rosco-* is unsuitable; he calls them *iridium aquoferrammines* and formulates them as $\text{Ir}(\text{NH}_3)_5(\text{H}_2\text{O})\text{X}_2$. Salts are described in which $\text{X}_2 = \text{Br}_2$, Cl_2 , and $(\text{NO}_2)_2$. The *chloride* $\text{Ir}(\text{NH}_3)_5(\text{H}_2\text{O})\text{Cl}_2$ is formed by boiling, for five hours, 5 g. $\text{Ir}(\text{NH}_3)_6\text{Cl}_3$ with 1½ times the calculated weight of KOH in 50 c.c. water, filtering, partially freezing the filtrate, adding 30 c.c. fuming HClAq , washing the pp. thus formed

with 22 p.c. cold HClAq and then with alcohol, dissolving in water, and again ppg. by conc. HClAq (for details v. *abstract in C. J.* 60, 1486 [1891]).

Iridium tribromide (vol. iii. p. 48). Compounds of this bromide with PBr₃ are described by Geisenheimer (*C. R.* 111, 40; *abstract in C. J.* 58, 1883 [1890]). By heating IrO₃·xH₂O with IrBr₃ and PBr₃, red needles of IrBr₃·3PBr₃ are formed; by heating this with PBr₃, black crystals of IrBr₃·2PBr₃ are produced.

Iridium tetrabromide (vol. iii. p. 48). Geisenheimer (*loc.*) describes the compound IrBr₃·2PBr₃, obtained by heating IrBr₃·3PBr₃ with PCl₅.

Iridium trichloride (vol. iii. p. 48). The following compounds with PCl₅ are described by Geisenheimer (*C. R.* 110, 1004; *abstract in C. J.* 58, 1068 [1890]). IrCl₃·3PCl₅; IrCl₃·2PCl₅; IrCl₃·PCl₅·2PCl₅.

Various compounds of IrCl₃ with H₃PO₄ and H₂PO₃, and salts of these, are also described. G. (*C. R.* 110, 1336; *abstract in C. J.* 58, 1069 [1890]) also describes the complex compounds 2IrP₂Cl₅·5AsCl₃ and IrCl₃·2PCl₅·2AsCl₃. For the salts IrCl₃·3KCl aq and IrCl₃·3MCl aq, v. Poly (*C. R.* 110, 1131; *abstract in C. J.* 58, 1067 [1890]). For a description of IrCl₃·3TiCl₃ aq, v. Lisony (*G.* 23 [1], 190; *abstract in C. J.* 64 [11], 880 [1893]). According to A. (*G.* 23 [1], 184; *abstract in C. J.* 64 [11], 879 [1890]), the passage of H₂S through a 2 p.c. solution of IrCl₃·3KCl produces pps. which are mixtures of Ir₂S₃ and IrS.

Iridium dioxide (vol. iii. p. 50). For methods of preparing IrO₂, v. Geisenheimer (*C. R.* 110, 865; *abstract in C. J.* 58, 948 [1890]).

Iridium disulphide (vol. iii. p. 50). IrS₂ is obtained by passing H₂S over IrCl₃·3LiCl at 4° to 7°, washing with absolute alcohol, and drying at 90° to 100° in a current of CO₂ (Antony, *G.* 23 [1], 190; *abstract in C. J.* 64 [11], 380 [1893]).

IRON (vol. iii. p. 51). Lockyer (*Pr.* 54, 359 [1893]) gives the emission spectrum obtained by using very fine electrolytically deposited iron as the poles of an electric lamp.

Properties and Reactions.—Iron volatilises in the electric furnace, using a current of 850 amperes and 50 volts (Moissan, *C. R.* 116, 1129 [1893]). Iron is superficially oxidised by heating to dull redness in NO (Sabatier a. Senderens, *C. R.* 114, 1429 [1892]); heated in NO₂ to c. 350°, reduced iron is oxidised with incandescence to Fe₂O₃ (S. a. S., *C. R.* 115, 236 [1892]; cf. *abstract in C. J.* 66 [11], 95 [1894]). Montemartini (*G.* 22, [1], 350) says that NH₃, N₂O, and N are formed by the solution of iron in excess of 27.5 p.c. HNO₃ aq (for quantities, v. *abstract in C. J.* 62, 1278 [1892]). For quantities of iron dissolved by HNO₃ aq of different concentrations, v. Gautier a. Charpy (*C. R.* 112, 1461; *abstract in C. J.* 60, 1496 [1891]).

Passivity of iron. Concerning the passivities of steel and wrought iron to HNO₃ aq, v. Andrews (*Pr.* 48, 116; 49, 481; *abstracts in C. J.* 60, 250, and 64 [11], 16 [1891 and 1893]).

Iron, bromochloride of. The compound FeBrCl was obtained by Lenormand (*C. R.* 118, 820; *abstract in C. J.* 64 [11], 877) by heating FeCl₃ with excess of Br in a sealed tube at c. 100°. The compound is opaque in thin

sections, and green by reflected light; very deliquescent; crystallises probably in hexagonal plates; easily sol. alcohol and ether, CS₂, &c., can be sublimed by heating in a tube containing a little Br.

Iron carbide. Arnold a. Read (*C. J.* 55, 798 [1894]) confirm the existence of Fe₃C in steel (v. Abel, *Proc. Inst. Mechan. Engineers*, 1885, 10; also Müller, *Stahl und Eisen*, No. 3); J. a. B. say that two forms of Fe₃C are found in steel.

Iron carbonyls. In 1891 Mond a. Quincke (*C. J.* 59, 604) obtained a compound of Fe with CO; further investigation of the reaction by Mond a. Langer (*C. J.* 69, 1090 [1891]) led to the isolation of two compounds.

Ferropentacarbonyl Fe₅(CO)₅. Mol. w. 195.55. V.D. at 142° ± 93.2, S.G._{15°} = 1.4604; distils completely, without decomposition, at 102.8° under 749 mm. pressure; solidifies at -21°.

Preparation.—FeC₂O₄ ppd. by adding a slight excess of K₂C₂O₄ aq to hot FeSO₄ aq, is well washed, and dried at 120°; it is then heated in a slow stream of H₂, temperature being raised until the substance in the tube is black, and then kept constant until gas ceases to come off, when the current of H₂ is stopped; the product is allowed to cool in H₂, placed in water without coming into the air, and treated with successive quantities of boiling water until sulphate is removed; it is then quickly dried on plates of gypsum, placed in the combustion tube, heated to c. 300° in H₂ till quite dry, and allowed to cool in H₂. The tube is then connected with a gas-holder containing CO, and the H₂ is completely displaced by CO; one end of the tube is then sealed, and the open end is kept in connection with the supply of CO. After 24 hours the tube is heated to c. 120°, while a slow current of CO is passed through it, and the issuing gases are passed through a tube kept at -20°. When iron carbonyl ceases to come over, the tube is let cool, and is then again put in connection with the CO supply. These processes are repeated many times; the daily yield of the carbonyl is not more than c. 1 g. from 100 g. iron.

Properties.—A pale-yellow, somewhat viscous liquid; unchanged in the dark, but in sunlight gives solid Fe₂(CO)₉ (v. *infra*); slowly decomposed on exposure to air, giving chiefly Fe₂O₃·xH₂O; completely decomposed at 180° to Fe and CO; soluble in EtOH, Et₂O, C₂H₄, mineral oils, &c. (For S.G., V.D., &c., v. *supra*). Fe(CO), it is not acted on by dilute H₂SO₄ aq, HClAq, or HNO₃ aq at the ordinary temperature; but is rapidly decomposed to Fe(NO)₃ aq, FeCl₃ aq, or FeBr₃ aq by conc. HNO₃ aq, ClAq, or Br₂ aq.

Diferroheptacarbonyl Fe₂(CO)₇. Obtained by exposing Fe(CO)₅ in a sealed tube to sunlight for some hours, collecting the solid that forms, washing with ether, and drying over H₂SO₄ for a short time. Yellow, lustrous flakes; gradually decomposed by exposure to air, turning brown. Not acted on by H₂SO₄ aq or HClAq at the ordinary temperature; decomposed by HNO₃ aq, Cl₂ or Br.

Iron carbonyls seem to be present in water-

also sometimes in compressed coal-gas. See a Scudder, *C. J. Proc.* 1891. No. 101).
Ferrous chloride (vol. iii. p. 53). Chasse-
 rant (*A. Ch.* [6] 30, 5, [1893]) describes the
 double salts $\text{FeCl}_2 \cdot 2\text{AmCl}$, $\text{FeCl}_2 \cdot \text{LiCl}$, 3aq , and
 $\text{FeCl}_2 \cdot 2\text{KCl}$.

Ferric chloride (vol. iii. p. 54). By deter-
 mining the rise of b.p. of alcohol and ether when
 FeCl_3 is dissolved in these solvents, Müller
 (*C. R.* 118, 644; abstract in *C. J.* 66 [11], 282
 [1894]) finds that the molecular formula of the
 chloride in these solutions is FeCl_3 . $\text{FeCl}_3 \cdot \text{aq}$
 reacts with many metallic sulphides, when
 heated therewith in sealed tubes; $\text{FeCl}_3 \cdot \text{aq}$, S ,
 and a chloride of the metal of the sulphide are
 generally formed (Cammerer, *C. C.* 291 [11],
 370; abstract in *C. J.* 62, 18 [1892]). Seibert
 a. Dorner (*Zeit. f. anorg. Chemie*, 5, 339, 41;
 v. abstracts in *C. J.* 66 [11], 140, 190 [1894]) have
 made a full investigation of the interaction
 of $\text{FeCl}_3 \cdot \text{aq}$ and KIAq ; their results are in
 keeping with the hypothesis that the direct re-
 action $\text{FeCl}_3 \cdot \text{aq} + \text{KIAq} = \text{FeCl}_2 \cdot \text{aq} + \text{KClAq} + \text{IAq}$
 is counterbalanced by the reverse reaction
 $\text{FeCl}_2 \cdot \text{aq} + \text{KClAq} + \text{IAq} = \text{FeCl}_3 \cdot \text{aq} + \text{KIAq}$.
 S. a. D. think that the first stage of the re-
 action is to produce an iodochloride; thus
 $\text{FeCl}_3 \cdot \text{aq} + \text{KIAq} = \text{FeICl}_2 \cdot \text{aq} + \text{KClAq}$; that this
 then decomposes, more or less completely
 (according to conditions of concentration, time,
 temperature, and mass), into $\text{FeCl}_2 \cdot \text{aq}$ and IAq ;
 and that $\text{FeCl}_2 \cdot \text{aq}$ and probably $\text{FeCl}_3 \cdot \text{aq}$ are
 re-formed until equilibrium is established.
 S. a. D. do not agree with the explanation of the
 mechanism of the reaction given by Carnegie
 (v. vol. iii. p. 55). Roozeboom (*Z. P. C.* 10, 477
 [1892]) has investigated the conditions of equi-
 librium in aqueous solution of the hydrates of
 FeCl_3 ; he has isolated hydrates $2\text{FeCl}_3 \cdot x\text{H}_2\text{O}$
 where $x = 4, 5, 7$, and 12. (For details, v.
 abstract in *C. J.* 64 [11], 119 [1893]). For a
 study of the interaction of $\text{FeCl}_3 \cdot \text{aq}$ and
 oxalic acid, v. Lemoine, *C. R.* 116, 981 (abstract
 in *C. J.* 64 [11], 405 [1893]). A compound of
 FeCl_3 with nitrosyl chloride, $\text{FeCl}_3 \cdot \text{NOCl}$, was
 obtained by Sudborough (*C. J.* 59, 660 [1891]),
 by immersing iron in liquid NOCl , and letting
 the liquid stand over H_2SO_4 ; the compound
 forms small golden-brown, deliquescent crystals
 (cf. vol. iii. p. 56; *Combinations*, No. 7).

Ferrus fluoride (vol. iii. p. 56). FeF_2 was
 obtained by Poulenc (*C. R.* 115, 941; abstract
 in *C. J.* 64 [11], 122 [1893]) by passing an-free
 HF over red-hot iron or dry FeCl_3 ; small, white,
 rhombic prisms; S.G. 4.09; decomposed by
 heating with H_2SO_4 , Na_2CO_3 , steam, air, HCl ,
 or H .

Ferric fluoride (vol. iii. p. 56). Poulenc (*l.c.*)
 obtained FeF_3 , in small, very refractive, greenish
 crystals, S.G. 3.87, by passing HF over red-hot
 iron, Fe_2O_3 , $\text{FeF}_2 \cdot \text{aq}$, or FeCl_3 ; also by dropping
 $\text{FeF}_2 \cdot \text{aq}$ into fused AmCl and heating in a cur-
 rent of an inert gas. FeF_3 does not fuse at
 1000° ; but is decomposed by heating in air, also
 by fusion with Na_2CO_3 , by heating in steam, or
 with HCl or H_2SO_4 . According to Sperafsky
 (*J. R.* 24, 304; abstract in *C. J.* 64 [11], 314
 [1893]), $\text{FeF}_3 \cdot \text{aq}$ shows a very small electrical
 conductivity; there is, therefore, no appreciable
 electrolytic dissociation; as the solution scarcely
 effects any inversion of cane sugar, S. concludes

that there is practically no hydrolytic dissociation.
 Cryoscopic determinations showed that
 the molecules in a dilute aqueous solution are
 chiefly FeF_3 , but indicated the existence of Fe_2F_7
 in more conc. solutions.

Iron, nitrides of (vol. iii. p. 59). Fowler
 (*C. N.* 68, 158 [1893]) obtained Fe_3N by heating
 reduced iron in a rapid stream of NH_3 . (For
 details v. abstract in *C. J.* 66 [11], 50 [1894]).

Ferric oxide (vol. iii. p. 61; also p. 57 for
 hydrates). At 1750° Fe_2O_3 is completely changed
 to Fe_3O_4 (Read, *C. J.* 65, 313 [1894]); in the elec-
 tric furnace Fe_2O_3 is formed, partly melted and
 partly crystallised (Moissan, *C. R.* 115, 1034
 [1892]). According to J. van Bemmelen a.
 Klobbie (*J. pr.* [2] 46, 497 [1893]), crystallised
 $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is obtained by treating with water the
 hexagonal crystals of $\text{Fe}_2\text{O}_3 \cdot \text{Na}_2\text{O}$ formed by
 heating Fe_2O_3 for some time with conc. NaOHaq ;
 the crystalline $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is not hygroscopic;
 H_2O is given off below 100° .

Iron, oxychlorides of (vol. iii. p. 62). Rousseau
 (*C. R.* 110, 4032; 113, 643; 116, 392; abstracts
 in *C. J.* 58, 1093 [1890]; 62, 119 [1892]; 64 [11]
 280 [1893]) describes compounds $x\text{FeCl}_2 \cdot y\text{Fe}_2\text{O}_3$,
 some crystalline and some amorphous, formed by
 heating $\text{FeCl}_2 \cdot \text{aq}$ at different temperatures, and
 also by the interaction of FeCl_2 and steam.

LANTHANUM (vol. iii. p. 116). Betendorff
 (*A.* 256, 159 [1890]) obtained the value 438.23
 for the at. w.; and Brauner (*B.* 24, 1378 [1891])
 the value 138.21 (0 - 16).

Winkler (*B.* 24, 873 [1891]) obtained results,
 by heating La_2O_3 with Mg in H , which pointed
 to the existence of a hydride of La (cf. Brauner,
l.c.).

LEAD (vol. iii. p. 122). The molecule in
 dilute solution in tin is probably monatomic
 (Heycock a. Neville, *C. J.* 57, 376 [1890]). The
 m.p. of lead was found by Griffiths a. Calendar
 (using a Pt thermometer) to be 327.69° (*C. N.*
 63, 1 [1891]). Lehmann (*Z. K.* 17, 274 [1890])
 says that lead separated electrolytically by a
 weak current, crystallises in leadlets that are
 probably monosymmetric, but that the crystals
 are regular octahedra when separated by a
 strong current. Veley (*S. C. I.* 10, 206; sum-
 mary of conclusions in *C. J.* 62, 410 [1892]) has
 examined the interaction of lead and nitric acid:
 an acid of intermediate concentration acts most
 rapidly; when HNO_2 is present the action in-
 creases. Montemartini (*G.* 22, 384, 337, 426
 [1892]) found that a little NH_3 was produced,
 especially with dilute $\text{HNO}_3 \cdot \text{aq}$. Lead rapidly
 oxidises to PbO when heated in NO ; oxidation
 occurs at $c. 200^\circ$ in NO_2 , with formation of a
 basic nitrate (Sabatier a. Senderens, *C. R.* 114,
 1429 - 115, 236 [1892]).

Lead, bromide of (vol. iii. p. 125). Several
 double compounds of PbBr_2 with alkali bromides
 have been described. For $\text{PbBr}_2 \cdot \text{AmBr}$, aq and
 $2\text{PbBr}_2 \cdot \text{AmBr}$, v. Wells a. Jolman, *Am. S.* [8]
 46, 25 (abstract in *C. J.* 63 [11], 523 [1893]); for
 $\text{PbBr}_2 \cdot \text{KBr}$, aq and $\text{PbBr}_2 \cdot 2\text{KBr}$, aq , v. Herty,
Am. 15, 357 (abstract in *C. J.* 66 [11], 465
 [1894]); for $2\text{PbBr}_2 \cdot \text{RbBr}$ and $2(\text{PbBr}_2 \cdot 2\text{RbBr})$, aq
 v. Wells a. *Am. S.* [8] 46, 34 (abstract in *C. J.* 66
 [11], 324 [1893]); and for K_2PbBr_4 , aq and
 $\text{K}_2\text{Pb}(\text{Br})_4$, 4aq , v. Wells, *l.c.* p. 190 (abstract,
l.c. p. 524).

Lead, chlorides of (vol. iii. p. 125). The statement, on p. 125 (vol. iii.), that only one chloride has been isolated is no longer true; PbCl_2 was prepared by Friedrich in 1893.

Lead tetrachloride (vol. iii. p. 126). PbCl_4 has been obtained by Friedrich (*B.* 20, 1434; *abstract in C. J.* 64 [11], 415 [1893]; *cf. M.* 14, 505; *abstract in C. J.* 66 [11], 16 [1894]), by passing Cl into HClAq containing PbCl_2 in suspension, adding NH_4Cl to the solution thus obtained, separating and drying the compound $\text{PbCl}_2 \cdot 2\text{NH}_4\text{Cl}$ thus formed, adding it to conc. cooled H_2SO_4 , allowing the oily drops that formed to collect at the bottom of the vessel, and shaking these drops repeatedly (and thickly) with conc. H_2SO_4 . PbCl_4 is a transparent, yellow, very refractive liquid, fuming in moist air with formation of PbCl_2 and Cl ; it is unchanged in contact with cold conc. H_2SO_4 , but when heated with the acid it decomposes explosively to PbCl_2 and Cl ; when heated with conc. H_2SO_4 in a current of Cl , some PbCl_4 passes over, but at c. 105° explosion occurs. PbCl_4 has S.G. 3.18 at 0° ; at c. -15° it solidifies to a yellowish, crystalline mass. A hydrate is formed with a little water; but addition of mixed water produces HClAq and PbO_2 . By adding PbCl_2 to a little cooled conc. HClAq , a crystalline compound, probably $\text{PbCl}_2 \cdot 2\text{HCl}$, is formed.

Several double salts of PbCl_4 with alkali chlorides have been isolated. Classen & Zahorski (*Zeit. f. anorg. Chemie*, 4, 100) give the formula $2\text{PbCl}_4 \cdot 5\text{AmCl}$ to the salt formed by digesting PbCl_4 with liquid Cl and fuming HClAq , and adding AmCl ; but Friedrich (*loc. cit.*) says the compound is $\text{PbCl}_4 \cdot 2\text{NH}_4\text{Cl}$. For compounds $\text{PbCl}_4 \cdot 2\text{MCl}$, when $\text{M} = \text{NH}_4$, Cs , K , and Rb , v. Wells (*Ann. S.* [3] 46, 180; *abstract in C. J.* 64 [11], 523 [1893]); C. a. Z. (*loc. cit.*) describe compounds of PbCl_4 with the hydrochlorides of pyridine and quinoline (*abstract in C. J.* 64 [11], 46 [1893]).

Lead dichloride (vol. iii. p. 125). Several double compounds with alkali chlorides are described by Randall (*Ann.* 15, 494 [1893]); Wells & Johnston (*Ann. S.* [3] 46, 25 [1893]); and Wells (*loc. cit.* p. 34). The compounds are of the forms $\text{PbCl}_2 \cdot 2\text{MCl}$, $\text{PbCl}_2 \cdot 3\text{MCl}$, &c., and $2\text{PbCl}_2 \cdot \text{MCl}$ (v. *abstracts in C. J.* 64 [11], 523, 524 [1893]).

Lead, fluorides of (vol. iii. p. 127). Brauner (*C. J.* 65, 393 [1894]) has prepared the compound $\text{PbF}_2 \cdot 3\text{KF} \cdot \text{HF}$ in various ways; the simplest process being to dissolve $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$ (v. *REP OXIDE OF LEAD, Addenda, infra*) in conc. HFAq and add KF . By acting on this salt with conc. H_2SO_4 , B. obtained evidence of the formation of lead tetr. fluoride, PbF_4 , but he did not succeed in isolating the compound.

Lead, iodide of (vol. iii. p. 127). Several double compounds of PbI_2 with alkali iodides have been isolated by Wells & Johnston, and Herty (v. *References under LEAD, Bromine, p. 913*). For the compound $\text{PbI}_2 \cdot 2\text{MgI}_2 \cdot 10\text{aq}$, v. Otto & Drewes (*Ar. Ph.* 229, 179; *abstract in C. J.* 64 [11], 984 [1893]).

Lead iodobromide and iodochlorides (vol. iii. p. 128). Miss Field (*C. J.* 63, 540 [1893]) has described the compounds $2\text{PbI}_2 \cdot \text{PbI}_2$, $2\text{PbI}_2 \cdot \text{PbBr}_2$, and $6\text{PbCl}_2 \cdot \text{PbI}_2$.

Lead protoxide (vol. iii. p. 128). PbO is unchanged at c. 1750° (Read, *C. J.* 65, 818

[1894]). The hydrate $2\text{PbO} \cdot \text{H}_2\text{O}$ (v. *III. p. 128*) is obtained in large crystals by allowing a solution of PbO in KOHaq to cool in the air; CO is absorbed, and the hydrate is deposited in colourless, tetragonal crystals, $a:b:c = 1:1:2$. (Luedeking, *Ann.* 13, 120 [1891]).

Red oxide of lead (vol. iii. p. 130). Hutchinson & Pollard (*C. J.* 63, 1136 [1893]) have examined the reaction of Pb_2O_3 with glacial acetic acid, and have isolated lead tetrachloride $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_4$, melting at c. 175° , and decomposing a little above that temperature.

Note.—The formula $\text{PbO}(\text{OC}_2\text{H}_3\text{O})_2$ said to be assigned by Jacquelin to the salt obtained by him (vol. iii. p. 130, *dbl.* 2, line 28 from top; and p. 131, *col.* 2, line 24 from bottom) should have been given as $\text{PbO}(\text{C}_2\text{H}_3\text{O})_2$, old notation.

Plumbates (vol. iii. p. 132). Kassner (*Ar. Ph.* [3] 28, 109; *abstract in C. J.* 58, 561 [1890]) describes plumbates of Ba, Ca, and Sr. Regarding the dissociation of Ca plumbate, v. Le Chatelier (*C. R.* 117, 109; *abstract in C. J.* 64 [11], 524 [1893]).

Lead oxyiodides (vol. iii. p. 132). Gröger (*M.* 13, 510; *abstract in C. J.* 62, 1892) describes the compound $\text{PbO} \cdot \text{PbI}_2$.

Lead, salts of (vol. iii. p. 132). The salt $\text{Pb}(\text{O}_2\text{H})_2$ (v. *supra*, *Red oxide of lead*) belongs to the type PbX_2 , to which form PbCl_2 also belongs.

Lead, sulphide of (vol. iii. p. 151). According to Hannay (*C. J. Proc.* Nos. 139 and 141 [1894]), when air is passed into molten PbS , one half of the lead remains as lead, and one half is volatilised, and deposited as PbS ; H. accounts for this change by supposing the reaction to be $2\text{PbS} + \text{O}_2 = \text{Pb} + \text{PbS}_2\text{O}_3$, the volatile PbS_2O_3 being decomposed in the colder part of the apparatus to PbS and SO_2 .

Lead sulphobromide and sulphochloride (vol. iii. p. 133). Parmentier (*C. R.* 114, 298; *abstract in C. J.* 62, 685 [1892]) obtained the compounds $\text{PbS} \cdot \text{PbBr}_2$ and $\text{PbS} \cdot \text{PbCl}_2$ by dissolving the halides in their acids and shaking the liquids while H_2S was passed over the surfaces of the solutions.

LITHIUM (vol. iii. p. 147). Guntz (*C. R.* 117, 732 [1893]) recommends to use a mixture of equal weights of LiCl and KCl for the electrolytic preparation of the metal; the mixture melts at 450° and the m.p. decreases as electrolysis proceeds. (For details as to size of electrodes, strength of current, &c., v. *abstract in C. J.* 66 [11], 91 [1894].) Holt & Sims, *C. J.* 65, 445 [1894], find that traces of a peroxide are formed, along with Li_2O , by burning Li in O .

Lithium, amide of, LiNH_2 . Formed by gently heating clean Li in a stream of NH_3 until violent action ceases, and then heating to c. 400° until the reaction is finished. A white, crystalline, transparent solid; melts between 380° and 400° ; decomposes in cold water slowly, giving LiOHaq and NH_3 ; decomposed by heating in air, but without taking fire (Titherley, *C. J.* 65, 504 [1894]; q. v. for further reactions).

Lithium, bromide of (vol. iii. p. 150). The hydrates $\text{LiBr} \cdot \text{aq}$, where $x = 1$ and 2, are described by Bogorodsky (*J. R.* 25, 3.3 [1893]).

Lithium, chloride of (vol. iii. p. 150). For $\text{LiCl} \cdot \text{aq}$ and $\text{LiCl} \cdot 2\text{aq}$ v. Bogorodsky (*loc. cit.*). For the double compounds $\text{LiCl} \cdot \text{MCl} \cdot \text{aq}$, where

Mn-Ox. *Os. Fe. Mn. or Ni.* Chassevant (*C. R.* 113, 646; 115, 111; abstracts in *C. J.* 62, 118, 1278 [1892]).

Lithium fluoride of (vol. iii. p. 150). Poulenc (*Bt.* [3] 11, 15 [1894]) obtained LiF in regular octahedra by heating the amorphous fluoride with KHF₂ and KCl, and washing with water; sl. sol. water, insol. 95 p.c. alcohol; melts at c. 1000° in H₂, and partially volatilises at 1100°-1200°.

Lithium hydroxide of (vol. iii. p. 150). For the freezing-points of aqueous solutions of LiOH v. Pickering (*C. J.* 65, 899 [1893]).

Lithium nitride of. Ouvrard (*C. R.* 114, 120 [1892]) obtained a black solid, probably Li₃N, by heating commercial Li to dull redness in N₂.

Lithium oxides of (vol. iii. p. 151). Almost the only products of heating Li in O is Li₂O; only traces of a peroxide are formed (Holtz. *Sims*, *C. J.* 65, 443 [1894]).

Magnesium (vol. iii. p. 157). Burton a. Vorce (*Am.* 12, 219 [1890]) obtained the value 24.22 (O = 15.96) for at. w., by converting pure Mg into Mg(NO₃)₂ and this to MgO. The molecule of Mg in dilute solution in tin is probably monatomic (Heycock a. Neville, *C. J.* 57, 376 [1896]). Mg crystallises in holohedral hexagonal form, $a:b:c = 1.1:1.0202$, isomorphous with Zn and Be (*L. a. V., l.c.*).

According to Montemagni (*C.* 22, 381, 397, 426 [1892]), a considerable quantity of H is given off when Mg interacts with HNO₃ (c. 13 p.c.); the quantity of NH₃ formed increases with concentration of the acid up to 40 p.c. HNO₃, after which it decreases. Mg burns in NO at a dull red heat (Sabatier a. Senderens, *C. R.* 115, 236 [1892]). Giorgi (*G.* 21, 510 [1891]) says that Mg dissolves in water saturated with CO₂; that H is given off, and crystals of MgCO₃·3aq are deposited. For the interactions of Mg and chlorides v. Seufert a. Schmidt (*A.* 267, 216; abstract in *C. J.* 62, 776 [1892]). Winkler has made an extended examination of the interactions of Mg and oxides (*B.* 23, 44, 120, 772, 2642; 24, 873, 1966; abstracts in *C. J.* 53, 331, 451, 693, 1372 [1890]; 60, 801, 155 [1891]).

Magnesium bromide of (vol. iii. p. 159). Beketoff (v. abstract in *C. J.* 62, 762 [1892]) gives H.F. [Mg.Br] = 121,700. The double salt 2MgBr·PbBr₂·16aq is described by Otto a. Drewes (*Ar. P.* 229, 585; abstract in *C. J.* 62, 566 [1892]).

Magnesium chloride of (vol. iii. p. 159). Skinner (*C. J.* 61, 341 [1892]) gives the boiling-points of solutions of MgCl₂ in water and alcohol, from c. 4.5 to c. 14.5 p.c. MgCl₂.

Magnesium iodide of (vol. iii. p. 161). Beketoff (*l.c.*) gives H.F. [Mg.I] = 64,800.

Magnesium nitride of (vol. iii. p. 161). For description of an experiment to demonstrate the formation of Mg₃N₂ v. Merz (*B.* 24, 8,940; abstract in *C. J.* 62, 409 [1892]).

Magnesium oxide of (vol. iii. p. 161). MgO is unchanged at c. 1750° (Read, *C. J.* 65, 313 [1894]); heated in the electric furnace, it melts with a current of 70 volts and 350 amperes (Moissan, *C. R.* 115, 1034; *C. R.* 116, 1429 [1892-3]). Richards a. Rogers (*P. Am.* 4, 28, 360 [1893]) found that MgO, prepared by evaporating MgCO₃ or Mg, with HNO₃ and heat-

ing very strongly, retained c. 10 times its volume of gas, chiefly O and N.

Magnesium silicides of (vol. iii. p. 162). Regarding the formation of compounds by heating together Mg and Si, v. Winkler (*B.* 23, 2842; abstract in *C. J.* 58, 1873 [1890]).

MANGANESE (vol. iii. p. 177). Moissan (*C. R.* 116, 849 [1893]) obtained Mn containing 4 to 5 p.c. O, by fusing MnO with charcoal (keeping MnO in excess) by means of a current of 60 volts and 800 amperes. Prelinger (*M.* 14, 353; abstract in *C. J.* 66 [11], 49 [1894]) prepared pure Mn by fusing Mn amalgam (formed by electrolysis MnCl₂Aq using a cathode of Hg) in pure H₂.

Mn is described by P (*L.*) as a grey porous metal; unchanged in dry air; reacts slowly with cold, rapidly with warm, water; dissolves in NH₄Cl, giving off NH₃ and H₂; S.G. 7.4212 referred to water at 4°. Moissan (*C. R.* 116, 1429 [1893]) found that Mn volatilises readily in the electric furnace, using a current of 80 volts and 380 amperes. Montemagni (*C.* 22, 394, 397, 426 [1892]) says that the gaseous products of the interaction of Mn and HNO₃ are H₂, NH₃, N₂, and N₂O. Finely divided Mn reacts with CO at c. 400°, producing MnO and C (Guntz, *C. R.* 114, 115 [1892]).

Manganese alloys of. The presence of c. 5 p.c. Mn in iron or steel scarcely affects the properties, except by slightly increasing the tenacity and malleability; a very hard tool-steel is formed with c. 13 p.c. Mn. Alloys with iron containing from 7 to 30 p.c. Mn are extremely hard and tough.

Manganese amalgams of (vol. iii. p. 179). Prelinger (*M.* 14, 353; abstract in *C. J.* 66 [11], 49 [1894]) prepared Mn₂Hg, by passing a current from a cathode of Hg through saturated MnCl₂Aq to an anode of C, or Pt-Ir, in a porous vessel, washing in running water, squeezing out excess of Hg, and drying in H over CaCl₂. By heating gently in a stream of pure, dry H₂, pure Mn was obtained.

Manganous chloride (vol. iii. p. 179). Chassevant (*A. Ch.* [6] 30, 5 [1893]) describes several double salts of MnCl₂; viz. MnCl₂·AmCl₂·2aq, MnCl₂·2AmCl₂·aq, and MnCl₂·LiCl₂·3aq. For the double salts M.KCl·2aq, M.CsCl·2aq; M·2XCl·2aq, X = NH₄, Cs, Rb; 2M·MgCl₂·12aq (M = MnCl₂), v. Saunders (*Am.* 14, 127; abstract in *C. J.* 62, 780 [1892]).

Manganic chlorides (vol. iii. p. 180). Regarding the composition of the chloride in the solution obtained by dissolving MnO₂ in HClAq, v. Vernon (*P. M.* [5] 31, 469), and Pickering (*P. M.* [5] 33, 284) (abstracts in *C. J.* 62, 19, 687 [1892]).

Manganese peroxide (vol. iii. p. 183). Regarding the compositions of the hydrated oxides, approximately MnO₂·2aq, prepared by different methods, v. Gorceu (*Bt.* [3] 4, 16 [1891]). *C.* (*C. R.* 110, 877; abstract in *C. J.* 58, 946 [1890]) gives some details regarding the interaction of MnO₂·2aq and H₂O₂·aq. Heated in the electric furnace, MnO₂ melts, gives off O, and leaves MnO (Moissan, *C. R.* 115, 1034 [1892]). MnO₂ is said to be formed by heating MnO₂ to c. 400° in NO (Sabatier a. Senderens, *C. R.* 114, 1476 [1892]). McLeod (*C. J.* 65, 302 [1894]) has confirmed his former observation that O is

given off when MnO_2 and KClO_3 are heated together. Regarding compounds of MnO_2 with basic oxides, v. Rousseau (C. R. 112, 525; 114, 72; 116, 1060; abstracts in C. J. 60, 645 [1891]; 69, 569 [1892]; 64 [11], 416 [1893]).

Permanganates (vol. iii. p. 186). Regarding the interaction of permanganates with H_2O_2 , Gorgou (C. R. 110, 958; abstract in C. J. 58, 1062 [1890]). Klobb (*ibid.* [8] 3, 508; abstract in C. J. 58, 947 [1890]) describes compounds of NH_3 with permanganates of Cd, Cu, Ni, and Zn.

Barium permanganate BaMnO_4 (the formula is wrongly printed BaMnO_3 in vol. iii. p. 186). For the preparation of this salt from KMnO_4 and $\text{Ba(NO}_3)_2$, v. Muthmann (B. 26, 1016; abstract in C. J. 62 [11], 324 [1893]).

Calcium permanganate. The formula given on p. 186 of vol. iii. is wrong; it should be $\text{CaMnO}_4 \cdot 5\text{H}_2\text{O}$.

Potassium permanganate (vol. iii. p. 186). Tivoli (G. 19, 630 [1890]) gives the following as the reactions that occur when pure AsH_3 is passed into dilute KMnO_4 : (1) $2\text{KMnO}_4 + \text{AsH}_3 = \text{K}_2\text{HASO}_4 + \text{Mn}_2\text{O}_3 + \text{H}_2\text{O}$; (2) $2\text{KMnO}_4 + \text{AsH}_3 = \text{K}_2\text{HASO}_4 + 2\text{MnO}_2 + \text{H}_2\text{O}$.

Silver permanganate (vol. iii. p. 187). AgMnO_4 decomposes slowly at the ordinary temperature, rapidly at 100° , and very rapidly at 125° (Gorgou, C. R. 114, 912; abstract in C. J. 62, 942 [1892]).

Manganese sulphide (vol. iii. p. 188). The pp. produced by adding $(\text{NH}_4)\text{HSO}_4$ to an ammoniacal solution of a Mn salt, after washing in an atmosphere of H_2S and drying in CO_2 at 70° , is MnS ; S.G. $170^\circ = 3.55$. By heating to 300° – 320° , or by leaving in contact with $(\text{NH}_4)\text{HSO}_4$ for some days, the reddish MnS becomes green without changing its composition; the green form of MnS is crystalline, S.G. $170^\circ = 3.63$ (Antony a. Donniel, G. 23 [1], 560 [1892]).

MASRIUM. In 1892 (C. J. 61, 491) Richmond a. Husseinoff obtained indications of the existence of an element before unknown in specimens of Egyptian fibrous alums. The supposed new element gave reactions indicating analogies with Be, Ca, and Zn; the results obtained by decomposing the oxalate by heat led to the at. w. of c. 228. The authors suggested the name *masrium*, from the Arabic name for Egypt.

MERCURAMMONIUM COMPOUNDS (vol. iii. p. 206).

Mercurio-ammonium salts $\text{NH}_4\text{Hg}_2\text{X}$ (vol. iii. p. 207). Barfoed's conclusion that these supposed compounds are really mixtures of mercurio-compounds and Hg is confirmed by Pesci (G. 21 [11], 569 [1891]). The product of the interaction of HgCl_2 and NH_4Aq , described as *dimercurio-ammonium chloride* $\text{NH}_4\text{Hg}_2\text{Cl}$ in vol. iii. (p. 208), leaves azetlic Hg when treated with ammoniacal $(\text{NH}_4)_2\text{SO}_4$, according to P. When the reaction of HgCl_2 with NH_4Aq proceeds out of the light, P. says that the change is $2\text{HgCl}_2 + 4\text{NH}_4\text{Aq} = (\text{NH}_4)_2\text{Cl}_2\text{NH}_4\text{Cl} + 2\text{NH}_4\text{ClAq} + 2\text{H}_2$. Similarly the reaction of NH_4Aq with Hg_2SO_4 produces a double compound of dimercurio-ammonium sulphate $(\text{NH}_4)_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ and H_2 ; and

$(\text{NH}_4)_2\text{NO}_3$, NH_4NO_3 , and Hg are formed, according to P., when HgNO_3Aq is treated with NH_4Aq .

Mercurio-ammonium salts $\text{NH}_4\text{Hg}_2\text{X}$. Regarding the conditions of formation of compounds of mercurio-ammonium chloride $\text{NH}_4\text{Hg}_2\text{Cl}$ (vol. iii. p. 208) with HgCl_2 and $\text{NH}_4(\text{Hg}_2\text{O})\text{Cl}_2$, v. Balestra (J. 21 [11], 294; abstract in C. J. 62, 276 [1892]).

Dimercurio-ammonium salts $\text{NH}_4\text{Hg}_2\text{X}$ (vol. iii. p. 209). Pesci (G. 20, 485 [1890]) has examined the conditions of formation of various salts of this class, especially the *nitrate* $\text{NH}_4\text{Hg}_2\text{NO}_3$ and compounds of this with NH_4NO_3 . The *sulphate* $(\text{NH}_4)_2\text{SO}_4 \cdot 2\text{aq}$ was formed by saturating conc. NH_4Aq with HgSO_4 , allowing the solution to evaporate in an atmosphere of NH_3 over CaO , and collecting the first crop of crystals; various compounds of $(\text{NH}_4)_2\text{SO}_4$ with $(\text{NH}_4)_2\text{SO}_4$ are also described (v. abstract in C. J. 60, 268 [1891]).

MERCURY (vol. iii. p. 212). Heycock a. Noville's results (J. J. 57, 876 [1890]) show that some condensation from monatomic molecules perhaps occurs in dilute solutions of Hg in tin. For corrected tables of the vapour pressures of Hg for each 10° from 180° to 480° , and each 1° from 830° to 860° , v. Young (C. J. 59, 629 [1891]).

Jäger (W. 48, 209 [1893]) recommends to prepare pure Hg by converting Hg that has been distilled *in vacuo* into HgNO_3 and electrolysis a solution of the salt, using Pt as anode and distilled Hg as anode. Sherstone (F. J. 61, 452 [1892]) noticed that Hg adheres to glass when brought into contact with Cl, Br, or I. Montemartini (G. 23, 884, 397, 426 [1891]) finds that the amount of NO produced by the interaction of Hg and HNO_3 decreases as concentration of the acid increases; that NO_2 is produced with acid more conc. than 27.5 p.c. HNO_3 ; HgNO_3 is formed with 25 p.c. acid, but $\text{Hg(NO}_3)_2$ with 50 to 70 p.c. acid; no NH_3 is formed with 27 and 50 p.c. acid.

Mercuric bromide (vol. iii. p. 215). HgBr_2 boils at 325° , according to Freyer a. V. Meyer (Zeit. f. anorg. Chemie, 2, 1 [1892]).

Mercurous chloride (vol. iii. p. 215). Harris a. V. Meyer have re-determined the V.D. of calomel at 448° and 518° ; the value obtained was 117.5. H. a. M. obtained considerable quantities of Hg and HgCl_2 by allowing the vapours obtained by heating calomel to c. 465° to diffuse along a glass tube; also by heating calomel at 420° for half an hour in a distillation flask at 33 mm. pressure. By heating calomel to 540° – 560° , and bringing a piece of KOH, which had been heated to c. 250° , into the vapour, they noticed that the surface of the KOH at once became covered with yellow HgO ; they also found that a piece of gold leaf held for a moment in the vapour was amalgamated (if kept for some time in the hot vapour the yellow colour was restored). H. a. M. think their results leave no doubt that the vapour obtained by heating calomel is $\text{Hg} + \text{HgCl}_2$, and that the molecular formula of calomel is Hg_2Cl_2 .

The reaction of Hg_2Cl_2 with NH_4Aq gives $(\text{NH}_4)_2\text{Cl}_2\text{NH}_4\text{Cl}$ and Hg, according to Pesci (v. supra. MERCURIO-AMMONIUM SALTS).

Mercuric chloride (vol. iii. p. 217). HgCl_2 boils at 307° (Freyer a. V. Meyer, Zeit. f. anorg. Chemie, 2, 1 [1892]). The white substance

processes by the reduction of HgCl_2Aq with a silver photographic image, or with pulverulent Ag, is Hg_2AgCl , according to Jones (S. C. M. 12, 985; abstract in C. J. 66 [11], 188 [1894]).

Mercuric cyanide; for an account of the conditions of formation and properties of the double mercury-zinc cyanide, v. Dunstan (C. U. 62, 666 [1892]).

Mercury, haloid compounds of (vol. iii. p. 219). Wells (Am. S. [3] 44, 221; abstract in C. J. 64 [11], 68 [1893]) describes a number of double compounds of mercury and cesium halides; the compounds belong to the forms (1) Cs_2HgX_4 , (2) Cs_2HgX_6 , (3) $\text{Cs}_4\text{HgX}_{10}$, (4) CsHgX_3 , (5) CsHgX_5 , (6) CsHgX_7 ; X = Cl, Br or I; in some cases the total X atoms comprise two different halogens.

Mercury hydrosulphide; for experimental attempts to prepare a definite compound, v. Linder a. Pietsch (C. J. 61, 123 [1892]).

Mercury phosphide (vol. iii. p. 223). By heating Hg and P₄ in a sealed tube for many hours at 750°-800°, and removing HgI₂ by treatment with KIaq , Granger (C. R. 115, 229 [1892]) obtained Hg_3P_2 in lustrous, metal-like, hexagonal crystals, appearing red by transmitted light, and giving a brown powder. The compound gives Hg and P when heated; heated in air it burns; detonates when mixed with KClO_4 and struck; burns in Cl₂; dissolved by aqua regia.

Mercurous sulphide (vol. iii. p. 224). Antony a. Sestini (G. 24 [1], 193 [1894]) obtained a black powder by passing dry H_2S , diluted with CO_2 , over dry Hg_2Cl_2 or $\text{Hg}(\text{C}_2\text{H}_3\text{O}_2)_2$, kept at -10°; when freshly prepared the black powder was scarcely changed in dry HCl at -18°, but at a somewhat higher temperature (below 0°) Hg_2Cl_2 was quickly formed. The substance dissolved in cold K_2SAq or NaSAq , but when temperature rose above 0° the solution became turbid and ppd. Hg. A. a. S. think their results show that Hg_2S exists at low temperatures (abstract in C. J. 66 [11], 318 [1894]).

Mercury sulphochloride (vol. iii. p. 225). The compound $2\text{HgS} \cdot \text{HgCl}_2$ is formed, according to Colson (C. R. 115, 657 [1892]), by passing H_2S into a solution of HgCl_2 in dry benzene.

MOLYBDENUM (vol. iii. p. 421). Smith a. Maas (A. C. J. 15, 897 [1894]) obtained the mean value 95.85 (O = 15.96) for the at. w. of Mo, by heating Na_2MoO_4 in a current of dry HCl and weighing the NaCl that remained ($\text{MoO}_3 \cdot 2\text{HCl}$ and H_2O were formed and removed). Smith a. Oberholtzer (Zeit. f. anorg. Chemie, 2, 63 [1893]) say that a mixture of MoOC_2O_4 and $\text{Mo}(\text{CO})_6$ is formed by heating Mo to 150°-200° in COCl_2 ; and that $\text{Mo}_2\text{S}_2\text{Cl}_4$ is produced by heating Mo to wedness in S_2Cl_2 . Mo is said to ppt. Ag from AgNO_3Aq , Au from AuCl_3Aq , HgCl_2 and then Hg from HgCl_2Aq , and Cu from solutions of its salts (Smith, Zeit. f. anorg. Chemie, 1, 860 [1891]). Montemartini (G. 22, 884, 897, 426 [1891]) finds that no NH_3 is formed in the interaction of Mo and HNO_3Aq with from 8 to 70 p.c. HNO_3 ; the most vigorous action occurs with acid c. 50 p.c., but the whole of the metal is not oxidised to MoO_3 , a nitrate being probably formed; the gaseous products are NO and NO_2 , the quantity of NO decreasing as the concentration of the acid increases.

Molybdenum, carbides of. By heating a mixture of MoO_3 and charcoal in the electric furnace, Moissan (C. R. 116, 1235 [1893]) obtained a very hard carbide, containing from 9.77 to 9.9 p.c. C; S.G. 8.8.

Molybdenum sesquioxide (vol. iii. p. 431). Heating Mo_2O_3 in NO produces MoO_3 (Sabatier a. Senderens, C. R. 114, 1429 [1892]).

Molybdenum trioxide (vol. iii. p. 432). MoO_3 , partially volatilises, and is partially reduced to one of the blue oxides, at c. 1750° (Read, C. J. 65, 813 [1894]). According to Smith a. Oberholtzer (Zeit. f. anorg. Chemie, 4, 236 [1893]), the products of heating MoO_3 in HBr are (1) $\text{MoO}_3 \cdot 3\text{HBr}$, and (2) $\text{Mo}_2\text{O}_5\text{Br}_2$; when HI is used and the temperature kept at 105°-120°, a blue oxide Mo_2O_5 is formed; HBr at 300°-400° forms $\text{Mo}_2\text{O}_5\text{F}_2$ (v. abstract in C. J. 64 [11], 471 [1893]). Cammerer (Chem. Zeit. 15, 967; abstract in C. U. 62, 944 [1892]) says that $2\text{MoO}_3 \cdot \text{H}_2\text{O} \cdot \text{H}_2\text{O}$ is formed by boiling MoO_3 with H_2Oaq .

Molybdenum, oxybromides of (vol. iii. p. 433). Smith a. Oberholtzer (Zeit. f. anorg. Chemie, 4, 236 [1893]) describe $\text{Mo}_2\text{O}_5\text{Br}_2$, square plates, color of KMnO_4 . Formed, along with $\text{MoO}_3 \cdot 3\text{HBr}$, by heating MoO_3 in HBr.

Molybdenum, oxyfluorides of (vol. iii. p. 433). For the products of the interaction of MoO_3Cl_3 and NH_3 , v. Smith a. Lehner (Zeit. f. anorg. Chemie, 4, 374; abstract in C. J. 64 [11], 629 [1893]).

Molybdenum, oxyanide of. By dissolving MoO_3 in KCyAq , and adding a strong acid, Péchard (C. R. 118, 804 [1894]) obtained MoO_2Cy_2 . Easily decomposed by contact with acids; double compounds with KCy and AgCy are also described.

Molybdenum, oxyfluorides of (vol. iii. p. 433). For $\text{Mo}_2\text{O}_5\text{F}_2$, a white, crystalline, deliquescent solid, obtained by heating MoO_3 in HF at 300°-400°, v. Smith a. Oberholtzer (l.c.).

Molybdenum, thioclauride of. For $\text{Mo}_2\text{S}_2\text{Cl}_4$, v. S. a. O. (l.c. 5, 63).

Molybdates, and derivatives thereof (vol. iii. p. 423). For compounds of molybdates of NH_4 and K with SO_2 and SeO_2 , v. Péchard (C. R. 116, 1441; 117, 104; abstracts in C. J. 64 [11], 530 [1893]).

Permolybdates. By the reaction of $\text{H}_2\text{O}_2\text{Aq}$ with $\text{K}_2\text{MoO}_4\text{Aq}$, Péchard (C. R. 112, 720; abstract in C. J. 60, 988 [1891]) obtained potassium permolybdate K_2MoO_6 4aq; the corresponding NH_4 salt was also formed.

Arseno-molybdates (vol. iii. p. 425). For salts of this class, v. Friedheim (Zeit. f. anorg. Chemie, 2, 814; 6, 11, 27; abstracts in C. J. 64 [11], 283; 66 [11], 238 [1893-4]).

Iodomolybdates. A great many salts of the form $x\text{MoO}_3 \cdot y\text{I}_2 \cdot z\text{H}_2\text{O}$ are described by Blomstrand (Zeit. f. anorg. Chemie, 1, 10; abstract in C. J. 64 [11], 122 [1893]).

Phosphomolybdates (vol. iii. p. 426). Friedheim (Zeit. f. anorg. Chemie, 2, 276; 6, 11, 27; abstracts in C. J. 64 [11], 472; 66 [11], 288 [1893-4]) describes several salts of this class.

Fluomolybdates (vol. iii. p. 425). v. Piccini (Real. Acad. Lincei, 7 [1], 267; abstract in C. J. 62, 484 [1892]), and Mauro (l.c., 1892 [1], 194; abstract in C. J. 64 [11], 124 [1893]).

NICKEL (vol. iii. p. 498). The *sat. w.* has been re-determined (1) by Schützenberger, by reducing oxides of Ni in H₂ (C. R. 114, 1149 [1892]); (2) by Winkler, by estimating Cl in NiCl₂ prepared from electrolytically deposited Ni (Zeit. f. anorg. Chemie, 4, 10 [1893]). Schützenberger's values varied from 58.52 to 59.8; Winkler's mean value from the gravimetric determinations was 58.903, and from the volumetric determinations 58.910 (Cl = 35.37, Ag = 107.66). Krüss & Schmidt (Zeit. f. anorg. Chemie, 2, 235 [1892]) insist that the substance called nickel is not an element, but Winkler (l.c.) controverts this statement (v. abstracts in C. J. 64 [11], 469 [1893]). The molecule of Ni in dilute solution in tin is probably monatomic (Heycock & Neville, C. J. 57, 376 [1890]). Schützenberger (C. R. 113, 177 [1891]) says that a volatile compound is formed by passing dry HCl over finely divided Ni heated to a dull redness. Montmartini (G. 22 [1], 255; abstract in C. J. 62, 1278 [1892]) gives the quantities of NH₃, N₂O, N, and HNO₂ (no NO) produced by the reaction of excess of HNO₃Aq (27.5 p.c.) with Ni. Heated to 200° in NO, the oxide NiO is formed without any Ni₂O₃ (Sabatier & Sendgrens, C. R. 114, 1429 [1892]). By passing NO₂, diluted with N, over reduced Ni, nitro-nickel (v. Ni₂NO₂) is obtained; it resembles nitro-cobalt (v. abstract, p. 908) (S. a. S., Bl. [3] 9, 669 [1893]).

Nickel carbonyl Ni(CO)₄. (Nickel carbonyl, vol. iii. p. 501.) Mol. w. was confirmed by Mond & Nasini (Z. P. C. 8, 150 [1891]), by finding the depression of the freezing-point of benzene. S.G. 1.35613 at 0°, 1.27132 at 36° (water at 4° = 1); S.G. at b.p. = 1.25406; molecular volume = 186.04; critical temp. = 151°. For some reactions v. Berthelot (C. R. 112, 1343; abstract in C. J. 60, 1427 [1890]).

Nickel, chloride of (vol. iii. p. 501). A volatile substance, decomposed by heating, is said to be formed by passing dry HCl over dry NiCl₂ at dull redness (Schützenberger, C. R. 113, 177; v. abstract in C. J. 60, 1429 [1890]). Chassevant (A. Ch. [6] 30, 5 [1893]) describes the double compounds NiCl₂.AmCl.6aq and NiCl₂.K⁺Cl.3aq.

Nickel, fluoride of (vol. iii. p. 502). Poulenc (C. R. 114, 1426 [1892]) obtained amorphous NiF₂ by heating NiCl₂ with excess of NH₄F, and washing away NH₄Cl with boiling alcohol; by heating in HF to 1200°-1300°, the amorphous MF₂ became crystalline, forming green crystals, S.G. 4.63, not acted on by warm HNO₃Aq, HClAq, or H₂SO₄Aq. Heated in air, NiF₂ gives NiO; heated with S it gives NiS; and with H₂ it is reduced to Ni (for other reactions, v. abstract in C. J. 62, 1159 [1892]). The double salt NiF₂.KF is formed by heating NiCl₂ with KHF₂, and washing away KCl by water (P., C. R. 114, 746 [1892]).

Nickel monoxide (vol. iii. p. 502). NiO melts and forms green crystals in the electric furnace (Moissan, C. R. 115, 1034 [1892]). NiO occludes small quantities of N and O (Richards & Rogers, P. Am. A. 28, 200 [1893]).

Nickel sesquioxide (vol. iii. p. 502). Ni₂O₃ fuses, gives up all its O, and leaves Ni at c. 1750° (Read, C. J. 46, 313 [1894]).

Nickel peroxide (vol. iii. p. 503). Campbell & Trowbridge (J. Anal. and App. Chem. 7, 301;

abstract in C. J. 46 [11], 288 [1894]) conclude that an oxide with more O than Ni₂O₃ can be obtained by ppg. NiSO₄Aq by Na₂CO₃Aq in presence of Br at different temperatures.

Nickel monosulphide (vol. iii. p. 503). Regarding the oxidation of this salt in air, to NiSO₄.6NiO, &c., v. P. de Clermont (C. R. 117, 229; abstract in C. J. 64 [11], 528 [1894]).

NIYBIUM (vol. iii. p. 505). Nb₂O₅ has not changed at c. 1750° (Read, C. J. 45, 313 [1894]). Piccini (Zeit. f. anorg. Chemie, 2, 21 [1892]) has prepared potassium fluoroniobate K₂NbO₅.2KF.aq.

NITRAMIDE NO₂(NH₂). Thiele & Lachman (B. 27, 1909 [1894]) obtained this compound by throwing NO₂.NK.CO₂K (potassium nitro-carbamate) into a mixture of ice and excess of H₂SO₄, extracting with ether, and evaporating in a stream of air. Crystals in clear prisms, which melt at 72° with decomposition; decomposed instantly to N₂O and H₂O by alkalis, alkali carbonates, borax, or Na acetate.

NITRATES (vol. iii. p. 509). Rolsseau & Tite (C. R. 115, 174 [1892]) find that many basic nitrates are completely decomposed by heating with water at 150°-200°. Regarding the formation of basic nitrates of Cd, Ca, Ni, and Zn, v. R. a. T. (C. R. 114, 1184); Riban (C. R. 114, 1357); and Werner (C. R. 115, 1499); (abstracts in C. J. 62, 1156, 1157, 1276 [1892]).

NITRIC ACID (vol. iii. p. 517). Regarding the colours produced by diluting and fuming HNO₃Aq v. Marchlewski (B. 24, 3271 [1891]). For revised tables showing the composition of HNO₃Aq of different concentrations v. Lunge & Rey (S. C. I. 1891, 543). Regarding the magnetic rotations of HNO₃Aq v. Porkin (S. J. 63, 57 [1893]). Hall (Am. J. 3, 554) has examined the rate of production of H and O, and the effect on the concentration of the acid, by the slow and steady electrolysis of HNO₃Aq (abstract in C. J. 62, 680 [1892]). The interactions of HNO₃Aq with many metals have been examined by Montmartini (G. 22 [1], 250, 277, 384, 397, 426 [1891]; abstracts in C. J. 62, 1278, 1402 [1892]), Veley (S. C. I. 10, 206; and elsewhere), and others; the results are noted under various metals. Pickering (C. J. 63, 436 [1893]) has isolated the hydrates HNO₃.H₂O and HNO₃.3H₂O; the freezing-points of HNO₃Aq, from 1.82 to 86.19 p.c. HNO₃, are given by P.

NITROGEN (vol. iii. p. 556). S.G. of N (at 0° = 1) = 0.7209; 1 litre weighs 1.25749 g. (Rayleigh, P. 1, 53, 134 [1893]). $\mu_D = 1.2053$ at -190° (liquid N, containing 5 p.c. O) (Livinge & Dewar, P. M. [5] 46, 929 [1893]). Absorption coefficient in alcohol, v. Menrich (Z. P. C. 9, 455 [1892]). Diffusion in water, v. Duncanson & Hoppe-Seyler (Zeit. physiol. Chemie, 17, 147 [1893]).

Preparations of pure nitrogen. Threlfall (S. M. [5] 33, 1 [1893]) gives minute directions for preparing pure N by passing air and NH₃ over hot Cu, and absorbing traces of O by CrCl₃Aq; exact directions for preparing the CrCl₃Aq are given, and the paper contains numerous details regarding the purifications of the reagents used in the process.

Supposed allotropic form of nitrogen. Threlfall (l.c.) has repeated experiments on sparking extremely pure N (v. vol. iii. p. 557); no condensation occurred down to -10° and c. 8 mm.

pressure, but when Hg_2 is present a compound of N and Hg is formed (probably Hg_2N_2 , v. vol. iii. p. 221). Regarding the fixation of nitrogen by growing plants, v. Beyerinck, also Schloesing & Laurent (abstracts in C. J. 62, 1019, 1021 [1892]).

Nitrogen, hydrides of (vol. iii. p. 559).

Hydrazic acid N_2H_4 . For new methods of preparing N_2H_4 v. Curtius (B. 24, 3341; 26, 1263; abstracts in C. J. 62, 112; 64 [11], 463 [1892-3]). Wislicenus (B. 25, 2084 [1892]) has obtained N_2H_4 by the interaction of NH_3 and N_2O_3 . From 1 g. to 1 g. Na is heated in a stream of NH_3 , until all is converted into $NaNH_2$; a current of dry N_2O is then passed over the $NaNH_2$ at 150°-250° as long as NH_3 is given off ($2NaNH_2 + N_2O = NaN_3 + NaOH + NH_3$). By dissolving the product in water, filtering, decomposing by dilute H_2SO_4 , and distilling, N_2H_4 is obtained.

The following salts are described by Curtius (B. 24, 3341; abstract in C. J. 62, 112 [1892]): $(NH_4)_2N_2$, $Pb(N_2)_2$, HgN_2 , NaN_3 .

Nitrogen, iodides of (vol. iii. p. 560). Diiodamine, NH_2I , is the product of adding excess of NH_3 to a conc. solution of I in conc. $KIAg$; by suspending NH_3 in water, and adding an ammoniacal solution of $AgNO_3$ or Ag_2O , a black compound $NAgI_2$ is obtained which explodes when dry (Szuhay, B. 26, 1433; abstract in C. J. 64 [11], 568 [1893]; cf. Selivanoff, B. 27, 1012; abstract in C. J. 66 [11], 312 [1894]).

Nitrous oxide (vol. iii. p. 561). Ramsay & Shields (C. J. 63, 833 [1893]) give the m.p. of N_2O as -102.3° , and the b.p. as -89.8° . Villard (C. R. 118, 1096 [1894]) gives the following data for the S.G. of liquid N_2O : 1.015 at 0° , .885 at 5° , .850 at 10° , .804 at 17.5° , .720 at 26.5° , .640 at 32.9° , .605 at 34.9° , .572 at 36.3° . Livinge & Dewar (P. M. [5] 34, 205 [1892]) give

$$\mu_D - 1 = .2634, \text{ and } \frac{\mu^2 - 1}{(\mu^2 + 2)d} = .163 \text{ at } -90^\circ.$$

Smith (S. C. J. 11, 867; 12, 10 [1893]) says that a regular stream of N_2O is obtained by heating to 240° - 250° a mixture of 1 pt. dry $NaNO_3$ with c. 1½ pt. dry $(NH_4)_2SO_4$. By passing N_2O , mixed with a little H, over Pd black, the H is entirely converted to H_2O , with formation of N (Monte-martini, Real. Acad. Lincei, 7 [11], 219 [1892]).

Nitric oxide (vol. iii. p. 562). Very pure NO is obtained, according to Emich (J. 13, 73 [1892]), by the interaction of copper and a mixture of H_2SO_4 and HNO_3 . Emich (l.c. p. 78) finds that NO is completely decomposed to N and O by passing over nets of Pt or Pd wire kept very hot by an electric current. Emich (l.c. p. 86) says that NO and O unite after being dried by long contact with P_2O_5 ; but Baker (C. J. 65, 611 [1894]) finds that dry NO and dry O do not combine at the ordinary temperature. Regarding the reactions between NO and metals and metallic oxides, v. Salatierr & Senderens (C. R. 114, 1420; 1476; abstracts in C. J. 62, 1151, 1271 [1892]); results are noted under the different metals and oxides in Addenda.

Nitrogen dioxide (vol. iii. p. 565). For the reactions of N_2O_4 with various metals and oxides v. S. a. C. (J. R. 115, 286; abstract in C. J. 62, 1390 [1892]); results are noted under the different metals and oxides in Addenda.

Nitrogen tetroxide (vol. iii. p. 565). For preparation of N_2O_4 v. Cundall (C. J. 59, 1076 [1891]). O. (l.c.) has measured the dissociation of liquid N_2O_4 in $CHCl_3$ up to c. 26° ; Ostwald (C. J. 61, 242 [1892]) shows that the dissociation follows van't Hoff's law for dilute solutions.

Nitrous acid (vol. iii. p. 567). Regarding the formation of HNO_2 in solution in HNO_3 , v. Veley (P. 52, 27; abstract in C. J. 64 [11], 415 [1893]).

Hyponitrous acid (vol. iii. p. 568). Tanatar (J. R. 25, 342; abstract in C. J. 66 [11], 186 [1894]) prepared $Ag_2N_2O_2$ by adding CaO to fairly conc. KNO_3 in the ratio $CaO:KNO_3$, then an equivalent of solid $NH_4OH.HCl$, heating to 50° , letting stand for a few days at the ordinary temperature, filtering, acidifying with acetic acid, ppg. by $AgNO_3$, dissolving $Ag_2N_2O_2$ in HNO_3 (which leaves $AgCl$), and ppg. again by Na acet.

Osmium (vol. iii. p. 611). Os fuses readily in the electric arc in a carbon capsule; when fused it has a crystalline fracture, and scratches quartz, but is scratched by topaz (Joly & Vezes, C. R. 116, 577 [1893]).

Osmic acid (vol. iii. p. 610). Morah (a. Wischin (Zeit. f. anorg. Chemie, 3, 153; abstract in C. J. 64 [11], 380 [1893]) say that the black powder obtained by the interaction of OsO_4 and K_2OsO_4 (vol. iii. p. 645), when dried over P_2O_5 in *vacuo* till it ceases to lose weight, is osmic acid H_2OsO_4 . M. a. W. describe the compound as a sooty black powder, smelling of OsO_4 in moist air, but unchanged under water containing alcohol. By passing H_2S over H_2OsO_4 , a violent reaction occurs, and $OsO_3S.H_2O$ is formed. Heated with conc. HCl for many hours with a little alcohol, and evaporated, $OsCl_4$ was obtained; an alcoholic solution of this substance with $KClAq$ gave K_2OsCl_6 , and the filtrate yielded $OsCl_4$ 3nq; the substance $OsCl_4$ is therefore supposed by M. a. W. to be a mixture of $OsCl_4$ and $OsCl_3$. By heating H_2OsO_4 with $HIAq$, violet black crystals, probably OsI_4 , were obtained. No action occurs when Os is heated with I, or with Br.

Potassium osmiumate (vol. iii. p. 645). Joly (C. R. 112, 1442 [1891]) prepares this salt by dissolving 100 pts. OsO_4 in a solution of 100 pts. KOH in 50 pts. H_2O , keeping the solution at c. 40° , and adding 40 c.c. NH_3 ; after a time the brown liquid becomes colourless, and a yellow crystalline pp. is formed. J. gives the formula $KNOsO_4$ to this salt. Heated in *vacuo* it is rapidly decomposed above 200° , and at 440° almost all the N is given off, the solid products being K_2O , OsO_3 , and $KOsO_4$ (v. abstract in C. J. 60, 1433 [1891]).

Oxides (vol. iii. p. 658). Regarding the connections between the stability of oxides when heated and the periodic classification of the elements, v. Bailey (C. J. 65, 106, 321 [1894]).

Oxygen (vol. iii. p. 703). * Atomic weight of oxygen (vol. iii. p. 705). Dumas & Henderson (C. N. 37, 127, 139, 151, 184; abstract in C. J. 64 [11], 410 [1893]) from careful determinations made by passing H over hot CuO , and weighing the water and Cu produced, adopt the value 15.87 for the at. w. of O. By measurements of the combining volumes of O and H, combi

ning the results with Rayleigh's determination of the S.G. of O, Scott (Z. 184, 648 [1898]) got the value 15.862. The following values summarise the most recent determinations (v. D. a. H., l.c.), Cooke a. Richards, 15.868; Noyes, 15.885; Rayleigh (Pr. 45, 426 [1890]), 15.89; Keiser, 15.949; Ledue (C. R. 146, 1248 [1898]), 15.88; D. a. H., 15.97; Scott, 15.862. The value adopted in this Dictionary, 15.90, is almost certainly too high; the mean of the values obtained by C. a. R., N., R., D. a. H., and S., is 15.875.

The ratio of the combining volumes of O and H was determined by Scott (l.c.) to be 2.0024:1 (v. WATER, this vol. p. 861). S.G. of O referred to H = 15.882 (Rayleigh, Pr. 50, 448 [1892]). For an examination of the whole of the spectrum of O, v. Eisig (W. 61, 747: abstract in C. J. 66 [11], 265 [1894]). Livinge a. Dewar (P. M. [5]

84, 205 [1892]) determined $\frac{\mu-1}{d}$ to be $\times 1389$, and

$\frac{\mu^2-1}{(\mu^2+2)d}$ to be $\times 1265$, at -182° (cf. Olszewski a.

Witkowski; abstract in C. J. 64* [11], 853 [1893]). For diffusion of O in water, v. Duncanson a. Hoppe-Seyler (Zeit. physikalische Chemie, 17, 147 [1892]).

Regarding the division of O between H and O₂ when mixtures of these gases are exploded, v. Harker (Z. P. C. 9, 673 [1892]). Dry O does not combine with dry NO at the ordinary temperature (Baker, C. J. 65, 611 [1894]); nor with dry K or Na, even when these metals are distilled in the gas (Holt a. Sims, C. J. 65, 440 [1894]).

OZONE (vol. iii. p. 788). Regarding the conditions of ozonification of oxygen, v. Shenstone a. Pries (C. J. 68, 938 [1893]). Baker (C. J. 65, 611 [1894]) confirms the observation of Shenstone a. Cundall (C. J. 81, 610 [1887]) that dry O is ozonised as rapidly as moderately dry O.

PALLADIUM (vol. iii. p. 792). The at. w. of Pd has been re-determined (1) by Bailey a. Lamb (C. J. 61, 745 [1892]), by analyses of Pd(NH₄Cl)₂; (2) by Keller a. Smith (Am. 14, 423 [1892]), by electrolytically from a solution of Pd(NH₄Cl)₂ in NH₄Aq; (3) by Joly a. Leidió (C. R. 116, 146 [1893]), by electrolysis of K₂PdCl₄ in HClAq; (4) by Keiser a. Breed (Am. 16, 20 [1894]), by determining the ratio of Pd to Cl in Pd(NH₄Cl)₂. B. a. L. obtained the value 105.459; K. a. S. the value 106.35; J. a. L. the value 105.665; and K. a. B. the value 106.27 (Cl = 35.47; Ag = 107.66; N = 14.01; O = 15.96). The molecule of Pd in dilute solution in tin is probably monatomic (Heycock a. Neville, C. J. 67, 876 [1890]). Regarding the preparation of pure Pd, v. the memoirs referred to *supra*. Pd absorbs O at 450°, forming PdO (Neumann, M. 18, 40 [1892]), but when Pd sponge is heated in dry O till the weight is constant Pd₂O is formed (Wilm, B. 25, 220 [1892]). Heated to 1200° in NO, Pd sponge that has been saturated with H becomes incandescent and the NO is completely changed to H₂O and NH₃, but oxidation of the Pd does not occur (Sabatier a. Senderens (C. R. 114, 1429 [1892])). Regarding palladium sulphides, v. Petrenko a. Arisshenko (Zeit. f. anorg. Chem., 4, 247; abstract in C. J. 64 [11], 475 [1898]). Phosphopalladous compounds, PdCl₂PO₄ and

PdCl₂P(OH)₂, are described by Fink (C. M. 123, 176; abstract in C. J. 63, 1285 [1892]). Vases (C. R. 115, 111) describes polychlorine palladous-chloronitride K₂Pd(NO₃)₂Cl₂ (abstract in C. J. 63, 1284 [1892]).

PHOSPHATES (vol. iv. p. 106). Rosell a. Frank (B. 27, 62) say that P is obtained by heating Na₃PO₄ or any phosphate of Ca or Mg, with Al in a current of H₂.

Dipotassium-hydrogen-orthophosphate (vol. iv. p. 111). According to Staudenmaier (Zeit. f. anorg. Chemie, 5, 893 [1896]), K₂HPO₄ cannot be isolated. S. (l.c.) describes acid salts, K₃H₂(PO₄)₃, aq, K₂H₂(PO₄)₂, 2aq, and KH₂(PO₄)₂.

Thorium orthophosphates (vol. iv. p. 112). Velok (Zeit. f. anorg. Chemie, 6, 161 [1894]) obtained Th(HPO₄)₂ aq by adding dilute H₂PO₄Aq to ThCl₄Aq.

Sodium pyrophosphate (vol. iv. p. 114). For a study of the reaction of HClAq with Na₂P₂O₇, v. Watson (S. C. I. 11, 224; abstract in C. J. 64 [11], 272 [1893]).

ORTHOPHOSPHORIC ACID (vol. iv. p. 125). According to Watson (C. N. 68, 199 [1893]), H₃PO₄ is changed completely to H₂P₂O₇ at 255°-260°, and HPO₃ begins to form at 290°-300°.

PHOSPHORUS (vol. iv. p. 120). Regarding the action of light and heat on ordinary phosphorus, v. Retgers (Z. P. C. 5, 211; abstract in C. J. 66 [11], [1894]).

Phosphorus hydride (vol. iv. p. 136). PH₃ and O react at a low pressure to form H₂PO₂ (2PH₃ + 3O₂ = 2H₂PO₂); when the gases are allowed to diffuse with one another at less than 50 mm. pressure, the reaction is PH₃ + O = H₂ + HPO₂; slow oxidation at greater pressures proceeds approximately according to the equation 4PH₃ + 5O₂ = 2HPO₃ + 2H₂PO₃ + 2H₂ (H. J. van de Stadt, Z. P. C. 12, 822 [1893]). According to van de S., explosion occurs at a certain low pressure, and this pressure depends much on the amount of moisture present, the moisture preventing and retarding the explosion. Edvi (Z. P.-C. 12, 155 [1893]) has examined the rate of decomposition of PH₃ by heat. For the reaction of PH₃ with AgNO₃Aq v. Vitell (abstract in C. J. 64 [11], 206 [1893]).

Phosphoric oxide (vol. iv. p. 141). For details regarding the preparation of pure P₂O₅, and for methods of detecting traces of P in P₂O₅, v. Threlfall (P. M. [5] 35, 14 [1893]).

Phosphorus suboxide (vol. iv. p. 139). B. (B. 27, 1257 [1894]) thinks that P₂O is formed by the interaction of P₂O₅ and NH₃.

Phosphorus sulphides (vol. iv. p. 145). Helff (Z. F. C. 12, 490 [1893]) confirms the statement that there are no definite compounds P₂S and P₄S; by heating together red P and S, he obtained P₂S, P₃S, P₄S, and P₅S.

Phosphorus sulphoxide of (vol. iv. p. 145). Oüvrad (C. R. 125, 1801; abstract in C. J. 64 [11], 164 [1893]) obtained P₂S₂O by heating P₄ in H₂S at 110°-120°; also by evaporating a solution of the three elements in the proper proportion in CS₂, and heating the residue to 120° in an inert gas; also by dissolving P₄ in a solution of P₂S in CS₂. The compound crystallises from CS₂ in golden-yellow prisms; it is unchanged in dry air, but slowly decomposed in moist air, giving H₂S; a. sol. CHCl₃, CCl₄, EtOH, or Et₂O; burns at c. 800°, giving P₂O₅, SO₂, and S; at c. 800° in vacuum it

separates into I and P₂S₅; decomposed by hot water, and explosively by fuming HNO₃.

• Potassium hypophosphates (vol. iv. p. 163). Bansa (*Zeit. f. anorg. Chemie*, 6, 128 [1894]) describes many double salts of K₂H₂P₂O₄ with VHP₂O₄, where M = Cd, Co, Cu, Mn, Ni, or Zn; also double salts MK₂P₂O₄, where M = Co or Ni. The double salt K₂Na₂P₂O₄·2aq is also described (abstract in *C. J.* 66 [11], 279 [1894]).

• Thallium hypophosphates. Joly (*C. R.* 118, 649 [1894]) obtained the normal salt Tl₂P₂O₄ and the acid salt Tl₂H₂P₂O₄ (abstract in *C. J.* 66 [11], 282 [1894]).

PLATINATES (vol. iv. p. 281).

Sodium thioplatinates. Schneider has obtained the salts Na₂PtS₂ and Na₂S₂PtS₂PtS₂ (*J. pr.* [2] 48, 411 [1894]).

Platino-oxalates (vol. iv. p. 285). Regarding the constitutional formulae of the K salts, v. Werner (*Zeit. f. anorg. Chemie*, 3, 267), and Söderbaum (*ibid.* 6, 45 [1894]).

PLATINUM-AMMONIUM COMPOUNDS (vol. iv. p. 292). Petersen (*Z. P. C.* 10, 580 [1892]) finds, from cryoscopic determinations, that most of the formulae generally used for these compounds are molecular. For a discussion of the constitutions of several classes of these compounds, and for measurements of the electrical conductivities of aqueous solutions of some of them, v. Werner a. Molati (*Z. P. C.* 12, 35 [1893]).

POTASSIUM (vol. iv. p. 297). Holt a. Sims (*C. J.* 65, 492 [1894]) found that K became soft at 54.5°, and remained soft to 60.5°, whereat it became brittle; complete melting occurred at 62.5°. H. a. S. say that dry K may be distilled in dry Q without the formation of any compound of the two elements. They found the products of the oxidation of K to be K₂O, K₂O₂, and finally K₂O₃ (v. *Oxides, infra*). Mixtures of KNO₃ and KNO₂ were formed by oxidising K in NO and in the red oxides of N.

Potassium amide (vol. iv. p. 299). Titherley (*C. J.* 65, 504 [1894]) says that KNH₂ is white and wax-like, melting at 270°-272°. It may be distilled without change in H at 400°-500°. T. says that KNH₂ is not decomposed by heating at c. 400° in a silver boat; if a glass vessel is used, NH₃ is given off with some N₂ and H₂, and K silicate is formed; a small amount of decomposition occurs in a silver boat at c. 500°, and at a full red heat the amide distils with partial splitting up into its elements. For other reactions of KNH₂, v. T. (*l.c.*).

Potassammonium (vol. iv. p. 299). Joannis (*C. R. M.* 713 [1894]) finds that there is no reaction between N and N₂H₄K, he says that N₂O produces K₂H₂, NH₃, KOH, and N. For the action of O, v. J. (*C. R.* 116, 1370; abstract in *C. J.* 64 [11], 462 [1893]).

Potassium bromide (vol. iv. p. 299). The melting-point is given as 215° by V. Meyer a. Riddle (*B.* 26, 2443 [1893]).

Potassium chloride (vol. iv. p. 300). Melts at 766°, according to M. a. R. (*l.c.*).

Potassium hydroxide (vol. iv. p. 302). Melts at 1045° (M. a. R. *l.c.*).

Potassium iodide (vol. iv. p. 303). Melts at 126° (M. a. R. *l.c.*). Regarding the interaction of KIAq and FeCl₃aq, v. FERRIC COMPOUNDS, *addenda*, p. 913.

Potassium tri-iodide (vol. iv. p. 304). Jakovkin (*Z. P. C.* 13, 539 [1894]) has made an examination of the dissociation of KI₃ in aqueous solution to KIAq and IAq (abstract in *C. J.* 66 [11], 271 [1894]).

Potassium nitride (vol. iv. p. 304). The experiments of Titherley (*C. J.* 65, 518 [1894]) show that K₂N does not exist.

Potassium oxide (vol. iv. p. 304). Holt a. Sims (*C. J.* 66, 432 [1894]) failed to obtain the monoxide K₂O by any of the methods said to give this compound, but they say that when K₂O is kept at a red heat it loses O and gives a substance the composition of which approaches that of K₂O. By heating K in a fairly dry mixture of O and N, oxidation proceeded until K₂O was formed (dry O is without action on K); when kept in water-vapour K₂O gave off O, and formed F₂O; and by heating K in N₂O, H. a. S. obtained K₂O₂, which on exposure to air became K₂O.

RUBIDIUM.

Rubidium haloid compounds (vol. iv. p. 413). Wheelgr (*Ann. S.* [3] 46, 88 [1893]) has prepared double compounds of the forms 3RbX.AsX₃ and RbX.As₂O₃; and (*l.c.* p. 269) various compounds of RbX with SbX₃. For physical properties of various salts of Rb, v. Erdmann, *Ar. Ph.* 232, 3 (abstract in *C. J.* 66 [11], 351 [1894]).

SELENATES (vol. iv. p. 476). Basic salts of Co and Cu are described by Bogdan (*Bl.* [8] 9, 584; abstract in *C. J.* 66 [11], 16 [1894]); the compositions given are 4CoO.3SeO₃aq and 3CuO.2SeO₃·4aq.

SILICON CHLORIDES (vol. iv. p. 458). In B. 27, 1943 [1894] Gattermann a. Weimig detail the best conditions for preparing SiCl₄, SiHCl₃, and SiCl₃, from crude Si obtained by the interaction of SiO₂ and Mg powder (v. vol. iv. p. 455). SiCl₄ melts at -12°, with NH₃Aq it gives off H and forms SiO₂·xH₂O (O. a. W. *l.c.*).

Silicon octochloride Si₂Cl₈. Mol. w. 360.9. V. D. 187.7. Obtained by G. a. W. (*l.c.*) by fractionating crude Si chlorides; boils from 220° to 215°; does not solidify at -12°.

SILVER (vol. iv. p. 464). The molecule of Ag in dilute solution in tin is probably monatomic (Heycock a. Neville, *C. J.* 57, 376 [1890]). According to Lütke (*W.* 50, 678; abstract in *C. J.* 66 [11], 92 [1894]), thin deposits of Ag on glass, mica, &c., are allotropic forms of the metal. Regarding alloys of Ag with cadmium, v. Heycock a. Neville (*C. J.* 65, 65 [1894]); also Mylius a. Fromm (*B.* 27, 630 [1894]).

Silver chloride (vol. iv. p. 468). By the action of AgCl₂Aq on pulverulent silver, Jones (*S. C. I.* 12, 983; abstract in *C. J.* 66 [11], 188 [1894]) obtained the compound Ag₂HgCl₄.

SODIUM (vol. iv. p. 473). The molecule of sodium in dilute solution in tin is probably monatomic (Heycock a. Neville, *C. J.* 57, 376 [1890]). Holt a. Sims (*C. J.* 65, 440 [1894]) found that dry sodium may be distilled unchanged in dry O; in ordinary O the products are Na₂O and Na₂O₂. Heating to 180°-200° in a limited volume of N₂O forms Na₂O; heating in NO or the red oxides of N produces a mixture of NaNO₂ and Na₂O (H. a. S. *l.c.*).

Sodium amide (vol. iv. p. 475). Titherley (*C. J.* 65, 504 [1894]) describes NaNH_2 as a white, transparent solid, with a crystalline structure; softens at 149° and is completely melted at 255° to a colourless liquid. NaNH_2 is obtained in transparent, crystalline needles by heating Na in NH_3 at $3-400^\circ$, allowing the product to sublime through a narrow tube, and again subliming by warming gently. NaNH_2 decomposes at a red heat into Na, N, and H_2 . It does not give NaN_3 , as generally stated (T., l.c.); no decomposition occurs at $300-400^\circ$.

Sodium bromide (vol. iv. p. 476). Panfiloff (*J. R.* 25, 272 [1893]) obtained NaBr. 5aq by exposing conc. NaBrAq out of doors in winter in Russia; decomposed at -25° to the dihydrate and water.

Sodium iodide (vol. iv. p. 481). NaI. 5aq separates from a solution of 100 g. NaI in 50 c.c. water at -14° ; at -10° it gives NaI. 2aq and water (P., l.c.).

Sodium nitride (vol. iv. p. 482). NaN_3 is not formed by the interaction of Na or Na_2O and NH_3 , or Na and N, according to Titherley (*C. J.* 65, 507; cf. *Sodium amide, supra*).

Sodium monoxide (vol. iv. p. 482). Na_2O is formed by heating Na in a limited volume of O_2 at a temperature below 180° ; also by heating Na in a limited volume of N_2O at $180-200^\circ$ (Holt a. Spence, *C. J.* 65, 442 [1894]). Heated in excess of O_2 the peroxide Na_2O_2 is formed. H. a. S. say Na_2O is greyish white. NH_3 reacts with gently heated Na_2O to form NaNH_2 and H_2O (Titherley, *C. J.* 65, 510).

Sodium dioxide (vol. iv. p. 483). Na_2O_2 does not combine with O when heated therein (H. a. S., l.c.). Regarding the interaction of Na_2O_2 and an alcoholic solution of HCl , cf. Tafel (*B.* 27, 816 [1894]). For reactions of Na_2O_2 , cf. Poleck, *B.* 27, 2051 (abstract in *C. J.* 66 [11], 816).

STRONTIUM. For *Strontium carbide*, cf. Moissan, *C. R.* 118, 688 (abstract in *C. J.* 66 [11], 818 [1894]).

SULFATES (vol. iv. p. 567).

Chromium sulphate (vol. iv. p. 570). Double salts of $\text{Cr}(\text{SO}_4)_3$ and $(\text{NH}_4)_2\text{SO}_4$ are described by Klobb (*B.* [3] 9, 668; abstract in *C. J.* 66 [11], 95 [1894]).

Vanadium sulphates (v. this vol. pp. 847, 848, 850).

OXY-IMIDO SULPHONATES (vol. iv. p. 602). Divers a. Haga have published a lengthy communication on these salts in *C. J.* 65, 523 [1894].

SULPHUR (vol. iv. p. 606). For measurements of the viscosity of molten S at different temperatures, cf. Brunhes a. Dussy, *C. R.* 118, 1045 (abstract in *C. J.* 66 [11], 348 [1894]).

THALLIUM (vol. iv. p. 674). The molecule of Tl in dilute solution in tin is probably monatomic (Heycock a. Neville, *C. J.* 57, 374 [1890]).

Thallium tri-iodide TlI_3 . Wells a. Penfield (*Zeit. f. anorg. Chemie*, 6, 312; abstract in *C. J.* 66 [11], 318 [1894]) obtained this compound, in rhombic crystals, $a:b:c = 0.828:1:1.217$, by digesting TlI and I with alcohol and evaporating over H_2SO_4 .

